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# PROCEEDINGS

OF

# THE PHYSICAL SOCIETY

# OF LONDON.

JANUARY 1894.

## I. *On the Behaviour of an Air-Core Transformer when the Frequency is below a certain Critical Value.* By E. C. RIMINGTON*.

[Plates I. & II.]

IT is usually supposed in the case of a transformer whose primary is connected to terminals having an alternating potential-difference of constant value between them, that the apparent impedance of the primary is diminished on closing the secondary. Under certain conditions, however, this is not the case, as the following investigation will show.

Let $r_1$ be the resistance of the primary circuit ;
L its inductance ;
$r_2$ the resistance of the secondary circuit ;
N its inductance ;
M the mutual inductance between the two coils.

The coefficients of induction are assumed constant in the following investigation, a result that can only be obtained in practice when coils not containing iron cores are employed. A pure sine-function alternating P.D. is also assumed.

Let $p=2\pi n$, where $n$ is the frequency of alternation.

Let $e$ be the value of the P.D. at any instant $t$, and E its maximum value.

---

* Read October 27, 1893.

Let $c_1$ and $c_2$ be the currents in the primary and secondary circuits respectively, $C_1$ and $C_2$ being their maxima.

Let $I_1 = \sqrt{r_1^2+p^2L^2}$, the impedance of the primary ;
and $I_2 = \sqrt{r_2^2+p^2N^2}$, the impedance of the secondary.

We have the well-known equations :—

$$L\frac{dc_1}{dt}+M\frac{dc_2}{dt}+c_1r_1=e\,; \quad . \quad . \quad . \quad . \quad (1)$$

$$N\frac{dc_2}{dt}+M\frac{dc_1}{dt}+c_2r_2=0. \quad . \quad . \quad . \quad . \quad (2)$$

Differentiate (1) with respect to $t$, and multiply by N ; differentiate (2) and multiply by M ; then on subtraction we obtain

$$(LN-M^2)\frac{d^2c_1}{dt^2}+Nr_1\frac{dc_1}{dt}-Mr_2\frac{dc_2}{dt}=N\frac{de}{dt}. \quad . \quad (3)$$

Multiply (1) by $r_2$ and add to (3). This gives

$$(LN-M^2)\frac{d^2c_1}{dt^2}+(Nr_1+Lr_2)\frac{dc_1}{dt}+r_1r_2c_1=r_2e+N\frac{de}{dt}. \quad (4)$$

Similarly we obtain

$$(LN-M^2)\frac{d^2c_2}{dt^2}+(Nr_1+Lr_2)\frac{dc_2}{dt}+r_1r_2c_2=-M\frac{de}{dt}. \quad (5)$$

Now it is obvious, if the P.D. be a pure sine function and the coefficients constants, that the currents must also be pure sine functions differing only in phase from the P.D.

Assume *, then,

---

* This assumption will evidently give a particular solution to equation (4), viz. $c_1=C_1\sin pt$.

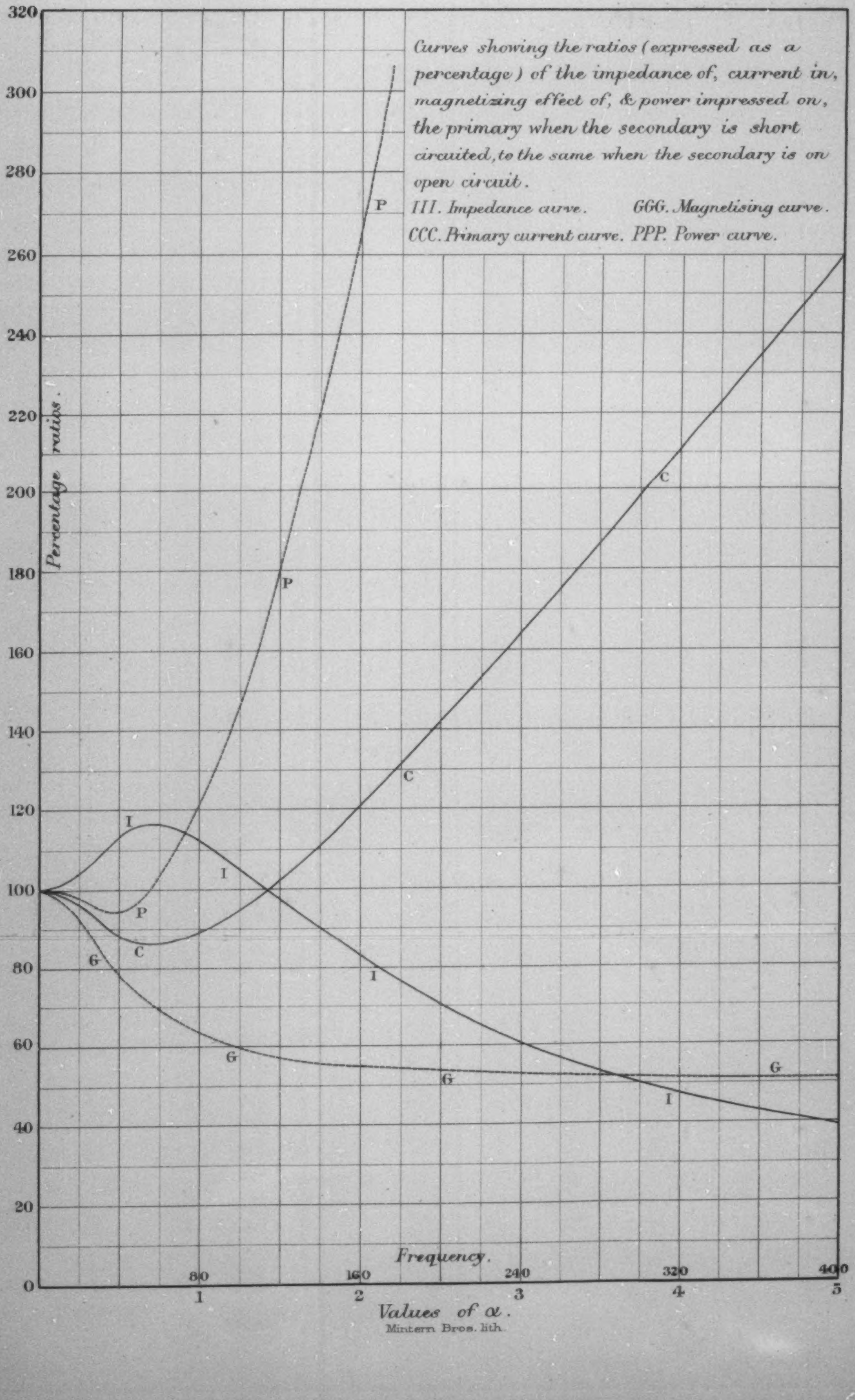
The complete solution is obtained by adding to this the solution of equation (4), assuming the right-hand member zero. So that the complete solution to (4) is

$$c_1=C_1\sin pt+Ae^{-\frac{k+h}{2}t}+Be^{-\frac{k-h}{2}t},$$

where
$$k=\frac{Nr_1+Lr_2}{LN-M^2},$$

and
$$h=\frac{\sqrt{(Nr_1-Lr_2)^2+4r_1r_2M^2}}{LN-M^2}.$$

The constants A and B depend on the phase of the P.D. at the instant the coil is switched on. The exponential terms (since they are both real and negative) rapidly die away, so that practically $c_1=C_1\sin pt$ after a short time has elapsed. The same remarks apply to the value of $c_2$.



*Curves showing the ratios (expressed as a percentage) of the impedance of, current in, magnetizing effect of, & power impressed on, the primary when the secondary is short circuited, to the same when the secondary is on open circuit.*

*III. Impedance curve. GGG. Magnetising curve.*

*CCC. Primary current curve. PPP. Power curve.*

Mintern Bros. lith.

$$c_1=C_1\sin pt,\quad c_2=C_2\sin(pt+\theta),\text{ and } e=E\sin(pt+\phi),$$

$$\frac{dc_1}{dt}=pC_1\cos pt\quad\text{and}\quad\frac{d^2c_1}{dt^2}=-p^2C_1\sin pt\,;$$

also $\dfrac{de}{dt}=pE\cos(pt+\phi)$.

Inserting these values in equation (4) gives

$$C_1[\{r_1r_2-p^2(LN-M^2)\}\sin pt+p(Nr_1+Lr_2)\cos pt]$$
$$=Er_2\sin(pt+\phi)+EpN\cos(pt+\phi).\quad .\quad .\quad .\quad (6)$$

For shortness, let

$a$ denote $r_1r_2-p^2(LN-M^2)$, and

$b$ denote $p(Nr_1+Lr_2)$.

Then (6) may be written

$$C_1\sqrt{a^2+b^2}\sin(pt+\psi)=EI_2\sin(pt+\phi+\chi),\quad .\quad (7)$$

where

$$\tan\psi=\frac{b}{a}\quad\text{and}\quad\tan\chi=\frac{pN}{r_2}.$$

As (7) must hold for all values of $t$, it follows that

$$C_1\sqrt{a^2+b^2}=EI_2,$$

or

$$C_1=\frac{EI_2}{\sqrt{a^2+b^2}},\quad .\quad .\quad .\quad .\quad .\quad .\quad (8)$$

and that $\psi=\phi+\chi$, or $\phi=\psi-\chi$.

Hence

$$\tan\phi=\frac{\frac{b}{a}-\frac{pN}{r_2}}{1+\frac{bpN}{ar_2}}=\frac{br_2-apN}{ar_2+bpN}=\frac{pL-\frac{p^3NM^2}{I_2^2}}{r_1+\frac{p^2r_2M^2}{I_2^2}}.\quad .\quad (9)$$

From (9) it is evident that the difference in phase between the primary current and the P.D. is always diminished on closing the secondary, since, when the latter is open

$$\tan\phi=\frac{pL}{r_1}.$$

In the same manner from (5) we obtain

$$C_2\sqrt{a^2+b^2}\sin(pt+\theta+\psi)=-pME\cos(pt+\phi)$$
$$=pME\sin\left(pt+\phi+\frac{3\pi}{2}\right).$$

Hence

$$C_2=\frac{pME}{\sqrt{a^2+b^2}}, \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and

$$\theta+\psi=\phi+\frac{3\pi}{2},$$

but

$$\psi=\phi+\chi.$$

Hence

$$\theta=\frac{3\pi}{2}-\chi=\pi+\left(\frac{\pi}{2}-\chi\right),$$

or $\theta$ is greater than $\pi$ and less than $\frac{3\pi}{2}$. Also

$$\tan\theta=\cot\chi=\frac{r_2}{pN}. \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Now from equation (8),

$$C_1=\frac{E}{\frac{\sqrt{a^2+b^2}}{I_2}}.$$

Call I the apparent impedance of the primary when the secondary is closed ($I_1$ is its impedance with secondary open). Then

$$I=\frac{\sqrt{a^2+b^2}}{I_2},$$

or

$$\begin{aligned} I^2I_2^2&=a^2+b^2\\ &=r_1^2r_2^2+p^4(LN-M^2)^2-2p^2r_1r_2(LN-M^2)\\ &\quad+p^2N^2r_1^2+p^2L^2r_2^2+2p^2r_1r_2LN\\ &=I_1^2I_2^2-p^2M^2\{p^2(2LN-M^2)-2r_1r_2\}, \end{aligned}$$

or

$$I^2=I_1^2-\frac{p^2M^2}{I_2^2}\{p^2(2LN-M^2)-2r_1r_2\}. \quad . \quad . \quad (12)$$

Equation (12) shows that I will only be less than $I_1$ when the quantity inside the brackets is positive; so that, if $2r_1r_2>p^2(2LN-M^2)$, $I^2$ is greater than $I_1^2$, and hence $I>I_1$, or the impedance of the primary is *increased* on closing the secondary.

For convenience let $\alpha_1=\frac{pL}{r_1}$, and $\alpha_2=\frac{pN}{r_2}$. $\alpha_1$ is of course the tangent of the angle of lag of the primary current behind the P.D. when the secondary is unclosed, while $\frac{\pi}{2}+\tan^{-1}\alpha_2$ is the phase-angle between the primary and secondary currents when the secondary is closed.

Let $M=\beta\sqrt{LN}$, so that $\beta$ represents the ratio of the magnetic induction passing through the secondary to that through the primary, and is of course less than unity, also $100(1-\beta)$ is the percentage magnetic leakage*. Substituting these values in (12) it becomes

$$\left(\frac{I}{I_1}\right)^2=1+\frac{\beta^2\alpha_1\alpha_2\{2-\alpha_1\alpha_2(2-\beta^2)\}}{(1+\alpha_1^2)(1+\alpha_2^2)} \quad . \quad . \quad . \quad (13)$$

To make $\frac{I}{I_1}$ greater than unity, obviously

$$\alpha_1\alpha_2 \text{ must be less than } \frac{2}{2-\beta^2},$$

---

* This is only the case when the two coils are equal in dimensions and similar in shape; otherwise the ratio of the total lines of magnetic induction through the secondary to those through the primary, when a current flows in the primary, will not be the same as the ratio of the lines through the primary to those through the secondary when there is a current in the latter.

$\beta$ is the geometrical mean of these two ratios. Thus: let $n_1$ be the number of turns in the primary and $G_1$ some constant depending on its shape and size, then the magnetic induction through the primary $=G_1n_1$, and $L=G_1n_1^2$. The induction through the secondary $=G_2n_2$, and $N=G_2n_2^2$, where the constant $G_2$ depends on the shape and size of the secondary. Let $\beta_1$ be the fraction of the primary induction that threads the secondary, and $\beta_2$ the fraction of the secondary induction that threads the primary. Then

$$M=G_1n_1\beta_1n_2=G_2n_2\beta_2n_1.$$

Hence $$M^2=\beta_1\beta_2G_1G_2n_1^2n_2^2,$$

or $$M=\sqrt{\beta_1\beta_2}\sqrt{LN};$$

so that $$\beta=\sqrt{\beta_1\beta_2}.$$

Also $$G_1\beta_1=G_2\beta_2, \text{ or } \frac{\beta_1}{\beta_2}=\frac{G_2}{G_1}.$$

So that for coils of the same shape and size,

$$\beta_1=\beta_2=\beta, \text{ since } G_1=G_2.$$

When the coils are of different shapes or sizes,

$$\frac{\beta_1}{\beta_2}=\frac{G_2}{G_1}=\frac{N}{L}\cdot\left(\frac{n_1}{n_2}\right)^2;$$

also if the number of turns in the primary and secondary is equal,

$$\frac{\beta_1}{\beta_2}=\frac{N}{L}.$$

or the critical value of

$$\alpha_1 = \frac{2}{\alpha_2(2-\beta^2)}\,;\ (\alpha_2\text{ given})\,;$$

and that of

$$\alpha_2 = \frac{2}{\alpha_1(2-\beta^2)}\,;\ (\alpha_1\text{ given}).$$

When the primary and secondary are identical or have the same shape and coil-volume *, and the secondary when closed is short-circuited,

$$\alpha_1=\alpha_2=\alpha.$$

Then

$$\left(\frac{\mathrm{I}}{\mathrm{I}_1}\right)^2 = 1 + \frac{\beta^2\alpha^2\{2-\alpha^2(2-\beta^2)\}}{(1+\alpha^2)^2}, \quad . \quad . \quad . \quad (14)$$

and the critical value of $\alpha=\sqrt{\dfrac{2}{2-\beta^2}}$.

When $\beta=1$, or there is no magnetic leakage, the critical value of $\alpha=\sqrt{2}$.

*To find the value of* $\alpha_1$ *that will make* $\dfrac{\mathrm{I}}{\mathrm{I}_1}$ *a maximum,* $\alpha_2$ *and* $\beta$ *being given.*

Obviously from (13) $\dfrac{\mathrm{I}}{\mathrm{I}_1}$ is a maximum when $\left(\dfrac{\mathrm{I}}{\mathrm{I}_1}\right)^2$ is a maximum, that is, when $\dfrac{\alpha_1\{2-\alpha_1\alpha_2(2-\beta^2)\}}{1+\alpha_1^2}$ is a maximum, since $\alpha_2$ and $\beta$ are constants.

Differentiating with respect to $\alpha_1$ and equating to zero gives

$$\alpha_1 = \frac{\sqrt{4+\alpha_2^2(2-\beta^2)^2}-\alpha_2(2-\beta^2)}{2}. \quad . \quad . \quad (15)$$

If $\beta=1$, or there be no magnetic leakage,

$$\alpha_1 = \frac{\sqrt{4+\alpha_2^2}-\alpha_2}{2} \quad \text{or} \quad \frac{\alpha_1}{1-\alpha_1^2} = \frac{1}{\alpha_2}. \quad . \quad (15\,a)$$

If the coils have the same time-constants, or $\alpha_1=\alpha_2=\alpha$,

$$\alpha = \frac{1}{\sqrt{3-\beta^2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (15\,b)$$

---

* Relative difference of thickness of insulation being supposed negligible, if different-sized windings are used.

and
$$\frac{I}{I_1}=\sqrt{1+\frac{\beta^2}{4-\beta^2}}=\frac{2}{\sqrt{4-\beta^2}}$$
if also $\beta=1$,
$$\alpha=\frac{1}{\sqrt{2}},\ \text{and}\ \frac{I}{I_1}=\sqrt{1\cdot\dot{3}}=1\cdot155.$$

Obviously, if $\alpha_1$ and $\beta$ are known the value of $\alpha_2$ that makes $\frac{I}{I_1}$ a maximum is by symmetry,
$$\alpha_2=\frac{\sqrt{4+\alpha_1^2(2-\beta^2)^2}-\alpha_1(2-\beta^2)}{2}\quad\text{or}\quad\frac{1-\alpha_2^2}{\alpha_2(2-\beta^2)}=\alpha_1,$$
or in the case of no magnetic leakage, $\frac{\alpha_2}{1-\alpha_2^2}=\frac{1}{\alpha_1}$.

If $\alpha_1$ and $\alpha_2$ are both variables, we have the two equations to be satisfied, viz.:—
$$\alpha_2=\frac{1-\alpha_1^2}{\alpha_1(2-\beta^2)}\quad\text{and}\quad\alpha_1=\frac{1-\alpha_2^2}{\alpha_2(2-\beta^2)},$$
$$\therefore\quad\alpha_1\alpha_2(2-\beta^2)=1-\alpha_1^2=1-\alpha_2^2,$$
$$\therefore\quad\alpha_1=\alpha_2=\alpha\ \text{say},$$
and
$$\alpha=\frac{1-\alpha^2}{\alpha(2-\beta^2)}\quad\text{or}\quad\alpha=\frac{1}{\sqrt{3-\beta^2}}.$$

So that to get $\frac{I}{I_1}$ a maximum, the primary and secondary should have the same value of $\alpha$, each equal to $\frac{1}{\sqrt{3-\beta^2}}$, or in the case of no magnetic leakage $=\frac{1}{\sqrt{2}}$; in which case $\frac{I}{I_1}$ will be 1·155, or a 15½ per cent. increase in impedance caused by short-circuiting the secondary, and this is the greatest that can be obtained.

Consider, then, the case of a transformer having coils with equal time-constants, and suppose there is no magnetic leakage.

For values of $\alpha$ below $\sqrt{2}$ the impedance is increased, and putting $\beta=1$ in equation (14) gives
$$\frac{I}{I_1}=\frac{\sqrt{1+4\alpha^2}}{1+\alpha^2}.$$

From this equation curve I I I, Plate I., has been plotted; the abscissæ are values of $\alpha$, and the ordinates values of $\frac{I}{I_1}$, expressed as percentages. For a transformer in which $\frac{L}{r_1}=\frac{N}{r_2}=\frac{1}{500}$ about, a second set of figures giving the frequency is also marked.

The curve C C C, Plate I., is the ratio of C the primary current when the secondary is closed to $C_1$ the same secondary open, and is evidently plotted from the equation

$$\frac{C}{C_1}=\frac{I_1}{I}=\frac{1+\alpha^2}{\sqrt{1+4\alpha^2}}.$$

*Power Distribution in above Transformer.*

Let P be the power impressed on the primary when the secondary is closed ;

$P_1$ the same when the secondary is open ;

H the heat-power developed in the primary when the secondary is closed ;

$P_2$ the power developed in the secondary.

Then

$$P=\frac{p}{2\pi}\cdot\frac{E^2I_2}{\sqrt{a^2+b^2}}\int_0^{\frac{2\pi}{p}}\sin pt\,.\sin(pt+\phi)\,.\,dt$$

$$=\frac{E^2(r_1I_2^2+r_2p^2M^2)}{2(a^2+b^2)}$$

$$=\frac{E^2}{2r_1}\cdot\frac{1+2\alpha^2}{1+4\alpha^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

$$H=\frac{p}{2\pi}\cdot\frac{E^2I_2^2r_1}{a^2+b^2}\int^{\frac{2\pi}{p}}\sin^2 pt\,.\,dt$$

$$=\frac{E^2I_2^2r_1}{2(a^2+b^2)}=\frac{E^2}{2r_1}\cdot\frac{1+\alpha^2}{1+4\alpha^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

$$P_2=\frac{p}{2\pi}\cdot\frac{(pME)^2r_2}{a^2+b^2}\int_0^{\frac{2\pi}{p}}\sin^2(pt+\theta)\,dt$$

$$=\frac{p^2M^2E^2r_2}{2(a^2+b^2)}=\frac{E^2}{2r_1}\cdot\frac{\alpha^2}{1+4\alpha^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Obviously $P=P_2+H$, unless there are masses of metal present, in which eddy currents are developed, or the frequency is so great that appreciable energy is radiated.

$$P_1=\frac{p}{2\pi}\cdot\frac{E^2}{I_1}\int_0^{\frac{2\pi}{p}}\sin pt\,.\sin(pt+\phi)\,dt$$

$$=\frac{E^2r_1}{2I_1^2}=\frac{E^2}{2r_1}\cdot\frac{1}{1+\alpha^2}. \qquad (19)$$

Hence, from (16) and (19),

$$\frac{P}{P_1}=\frac{(1+2\alpha^2)(1+\alpha^2)}{1+4\alpha^2}=\frac{1+3\alpha^2+2\alpha^4}{1+4\alpha^2}, \qquad (20)$$

and from this equation (20) the curve marked PPP (Plate I.) is plotted.

The curves for $P$, $H$, $P_2$, and $P_1$ are plotted in Plate II. for values of $\alpha$ up to 2.

### *Magnetizing Effect of the Coils.*

Let $g$ be the number of effective current-turns at any instant when the secondary is closed, and $G$ its maximum value.

Then
$$g=n_1c_1+n_2c_2,$$

where $n_1$ and $n_2$ are the number of turns in the primary and secondary respectively, and

$$G=\sqrt{n_1^2C_1^2+n_2^2C_2^2+2n_1n_2C_1C_2\cos\theta},$$

where $\theta$ is the phase-angle between the two currents.

If we assume the primary and secondary to occupy equal volumes, and we can neglect the relative difference in thickness of the insulation of the two coils, $\frac{n_1}{n_2}=\sqrt{\frac{r_1}{r_2}}$,

$$\therefore\ G=n_1\sqrt{C_1^2+C_2^2\frac{r_2}{r_1}+2C_1C_2\sqrt{\frac{r_2}{r_1}}\,.\cos\theta},$$

$$=\frac{n_1E}{\sqrt{a^2+b^2}}\sqrt{I_2^2+p^2M^2\frac{r_2}{r_1}-2p^2MN\sqrt{\frac{r_2}{r_1}}};$$

or (since $M^2$ is assumed $=LN$)

$$G=\frac{n_1 E r_2}{\sqrt{a^2+b^2}}=\frac{n_1 E}{r_1\sqrt{1+4\alpha^2}}.$$

Call $G_1$ the maximum value of $g$ when the secondary is open; then

$$G_1=\frac{n_1 E}{I_1}=\frac{n_1 E}{r_1\sqrt{1+\alpha^2}},$$

$$\therefore \quad \frac{G}{G_1}=\sqrt{\frac{1+\alpha^2}{1+4\alpha^2}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Evidently, then, the magnetizing effect is always diminished on closing the secondary.

The curve GGG (Plate I.) is plotted from equation (21).

It will be seen, on inspecting Plate I., that in the cases of the impedance-curve and the current-curve the critical value for $\alpha=\sqrt{2}=1{\cdot}414$, while the value of $\alpha$ that makes them a maximum and a minimum respectively is $\alpha=\frac{1}{\sqrt{2}}={\cdot}707$. This latter value of $\alpha$ is the critical value for the curve PPP, while, as may be seen by differentiating equation (20) and equating to zero, the value of $\alpha$ that makes this curve a minimum is $\frac{\sqrt{\sqrt{3}-1}}{2}$, or ·4278.

Consider, now, the case of primary and secondary having the same time-constants but with magnetic leakage.

Then we know the *critical value of* $\alpha=\sqrt{\frac{2}{2-\beta^2}}$.

The value of $\alpha$ to make $\frac{I}{I_1}$ a maximum from (15*b*) $=\frac{1}{\sqrt{3-\beta^2}}$.

Let $\gamma$ represent the ratio of the former value of $\alpha$ to the latter, then

$$\gamma=\sqrt{\frac{6-2\beta^2}{2-\beta^2}};$$

also the maximum value of $\frac{I}{I_1}=\frac{2}{\sqrt{4-\beta^2}}$.

From equation (11),

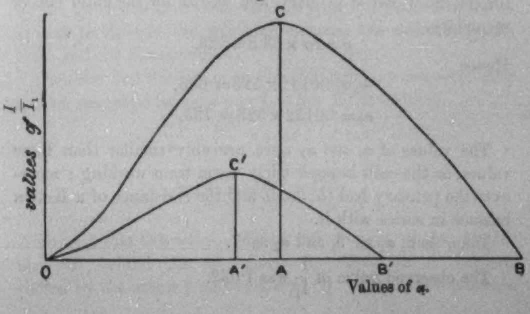
$$\tan\theta=\frac{r_2}{pN}=\frac{1}{\alpha};$$

and $\theta$ is the angle by which the secondary current is in advance of the primary, and it lies between $\pi$ and $\frac{3\pi}{2}$; it therefore follows that the angle by which the secondary current lags behind the primary lies between $\frac{\pi}{2}$ and $\pi$, and is $\frac{\pi}{2} + \tan^{-1} \alpha$. The following Table gives values of the above quantities for values of $\beta$ from 1 to ·1.

| $\beta$. | Critical values of $\alpha$. | Values of $\alpha$ for max. $\frac{I}{I_1}$. | $\gamma$. | Max. values of $\frac{I}{I_1}$. | Critical phase-angle. | Phase-angle for max. $\frac{I}{I_1}$. |
|---|---|---|---|---|---|---|
| 1·0 | 1·414 = $\sqrt{2}$ | ·707 = $\frac{1}{\sqrt{2}}$ | 2 | 1·155 | 144° 44′ | 125° 16′ |
| ·9 | 1·300 | ·676 | 1·920 | 1·120 | 142 26 | 124 4 |
| ·8 | 1·210 | ·650 | 1·865 | 1·090 | 140 26 | 123 2 |
| ·7 | 1·150 | ·630 | 1·825 | 1·070 | 139 0 | 122 13 |
| ·6 | 1·105 | ·615 | 1·795 | 1·050 | 137 51 | 121 36 |
| ·5 | 1·070 | ·605 | 1·770 | 1·032 | 136 56 | 121 11 |
| ·4 | 1·045 | ·595 | 1·760 | 1·020 | 136 16 | 120 45 |
| ·3 | 1·023 | ·586 | 1·750 | 1·010 | 135 39 | 120 22 |
| ·2 | 1·010 | ·581 | 1·740 | 1·007 | 135 17 | 120 10 |
| ·1 | 1·002 | ·578 | 1·730 | 1·001 | 135 4 | 120 2 |

It will be seen from the column of values for $\gamma$ that when $\beta=1$, or there is no magnetic leakage, the critical value of $\alpha$ is twice its value for maximum $\frac{I}{I_1}$; and the effect of leakage is to diminish this number, so that when $\beta = ·1$ it is reduced to 1·73. This is shown in the subjoined figure.

Fig. 1.



The curve OCB represents the critical part of the curve III (Plate I.) when there is no leakage, and A comes midway between O and B, so that $OA = \frac{1}{2} OB$; also $OB = \sqrt{2} = 1{\cdot}414$, $OA = {\cdot}707$, and, if the point O represent 100 divisions, $AC = 15\frac{1}{2}$ divisions.

The curve OC′B′ represents the critical part when $\beta = {\cdot}1$; $OB' = 1{\cdot}002$ and $OA' = {\cdot}578 = {\cdot}577 OB'$; also $A'C' = {\cdot}12$ division. Hence we see that the effect of magnetic leakage is to shift the point A′ corresponding to the maximum values of $\frac{I}{I_1}$ from midway between O and B′ and towards B′.

The author was enabled, through the kindness of Dr. Fleming, to try an experiment in the meter-testing room of the Electric Supply Company, using a Kelvin balance for measuring the currents through the primary coil. The alternating P.D. was obtained from the terminals of a transformer capable of giving over $100^A$; and as the maximum current ever taken was $6\frac{1}{2}^A$ about, the P.D. may be assumed constant. The frequency was 83·3.

The air-core transformer used for the experiment consisted of two coils wound one inside the other, and of No. 20 B.W.G. cotton-covered wire. The inner coil was used as primary and the outer as secondary.

Each coil consisted of 5 layers, of 125 turns per layer.

Calculating the time-constants or values of $\frac{L}{R}$ for the coils by Perry's approximate formula, they worked out as ·00121 for the inner coil or primary, and ·00152 for the outer coil or secondary.

$$p = 2\pi \times 83{\cdot}3 = 523.$$

Hence

$$\alpha_1 = {\cdot}00121 \times 523 = {\cdot}633,$$

$$\alpha_2 = {\cdot}00152 \times 523 = {\cdot}795.$$

The values of $\alpha_1$ and $\alpha_2$ were probably smaller than these values, as the coils became fairly warm from working; moreover the primary had the leads and the resistance of a Kelvin balance in series with it.

Take, then, $\alpha_1$ as ·5, and $\alpha_2$ as ·7.

The observed value of $\frac{I}{I_1}$ was 1·032.

Substituting these values in equation (13) makes $\beta = \cdot 57$, or a magnetic leakage of 43 per cent., if the P.D. were a true sine function. This seems a rather large value for the leakage; and it is probable that the leakage was considerably less than this, but that the P.D. was not a pure sine function, and on this account the ratio $\frac{I}{I_1}$ was less than it otherwise would have been.

The above experiment was only a rough one, but it showed an increase of 3·2 per cent. in the impedance of the primary on closing the secondary: moreover the time-constants of the coils were not suited for giving the best effect with the frequency employed; but, as is seen from the previous theoretical investigation, by employing a primary and a secondary having equal time-constants suitably related to the frequency, and a pure sine function P.D., an increase of impedance of from 10 to 12 per cent. ought to be obtained; 15½ per cent. increase could never be obtained in practice, as there must always be some magnetic leakage.

In transformers with iron cores this effect would be likely to escape notice, as the values of $\frac{L}{R}$ would be so large that the critical frequency would be very small, so that for all frequencies employed in practice the impedance of the primary would diminish on closing the secondary. The iron core would also distort the current from a pure sine function.

The above investigations may be with advantage treated by the geometrical or clock-face diagram method, as it shows at once to the eye the relations between the different quantities and the phase-angles.

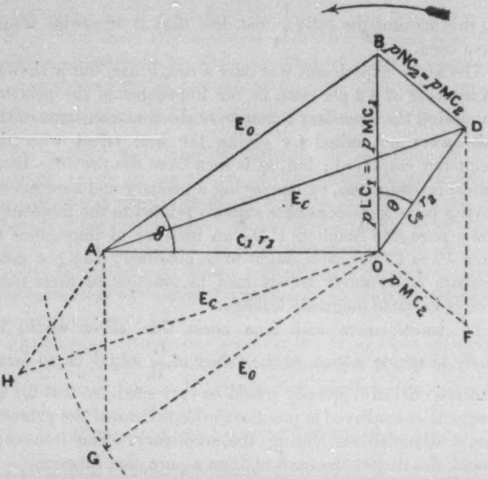
Consider first the case of an identical primary and secondary and no magnetic leakage; or $L = N = M$, and $r_1 = r_2$.

As before, call $\frac{pL}{r_1} = \frac{pN}{r_2} = \alpha$, and let $\tan^{-1}\alpha = \theta$, or

$$\tan\theta = \alpha = \frac{pL}{r_1} = \frac{pN}{r_2}.$$

Draw a line $OA = C_1 r_1$. Draw OB at right angles to OA and 90° behind OA as regards the direction of rotation, shown by the arrow; make $OB = pLC_1$. Then AB represents the value of the P.D. at the terminals of the primary when the secondary is open or of $E_0$, and its actual position on the diagram is the dotted line OG parallel to AB.

Fig. 2.



Now OB also represents $pMC_1$, since $M=L$. Draw OD making an angle $\theta$ (equal to the angle OAB) with OB and behind it; drop the perpendicular BD on to OD. Then OD represents $C_2 r_2$, and $BD=pNC_2=pMC_2$. Draw OF 90° behind OD and equal to $pMC_2=BD$. Then OF represents the back E.M.F. in the primary due to the mutual induction, the E.M.F. in the same due to self-induction being $OB=pLC_1$, and their resultant is obviously OD.

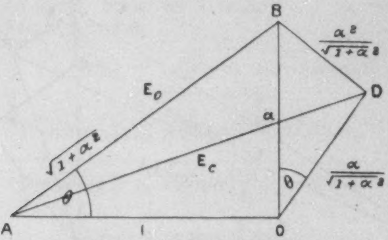
Join AD. Then AD must represent in magnitude and OH (equal and parallel to AD) in direction in the diagram the terminal P.D. when the secondary is closed or $E_c$, because $C_1 r_1$ or OA is the resultant of OH, the impressed P.D., and OD the resultant E.M.F. in the primary due to self and mutual inductions.

Now, as the diagram is drawn, $E_c$ is greater than $E_0$, the primary current being constant, so that if the terminal P.D. were kept constant the primary current with the secondary closed divided by the same with the secondary open would equal $\frac{E_0}{E_c}$, or the impedance ratio $\frac{I}{I_1} = \frac{E_c}{E_0}$.

The actual lines that need be drawn are shown in full, the dotted ones being superfluous except for explanation, and they will in future be omitted.

If we take $C_1 r_1$ equal to unity we shall have the diagram fig. 3.

Fig. 3.


B
$\frac{\alpha^2}{\sqrt{1+\alpha^2}}$
$E_0$
D
$\alpha$
$\sqrt{1+\alpha^2}$
$E_c$
$\theta$
$\theta$
$\frac{\alpha}{\sqrt{1+\alpha^2}}$
A
1
O

$$\text{Now } AD^2 = AO^2 + OD^2 - 2AO\,.\,OD \cos AOD$$

$$= 1 + \frac{\alpha^2}{1+\alpha^2} - \frac{2\alpha}{\sqrt{1+\alpha^2}} \cos\left(\frac{\pi}{2} + \theta\right)$$

$$= 1 + \frac{\alpha^2}{1+\alpha^2} + \frac{2\alpha}{\sqrt{1+\alpha^2}} \sin\theta.$$

Now $\tan\theta = \alpha$, hence $\sin\theta = \frac{\alpha}{\sqrt{1+\alpha^2}}$;

$$\therefore\ AD^2 = 1 + \frac{3\alpha^2}{1+\alpha^2} = \frac{1+4\alpha^2}{1+\alpha^2}, \text{ or } AD = \sqrt{\frac{1+4\alpha}{1+\alpha^2}}.$$

Now AD represents $E_c$ and AB represents $E_0$. So that

$E_c >=< E_0$ accordingly as $\sqrt{\frac{1+4\alpha^2}{1+\alpha^2}} >=< \sqrt{1+\alpha^2}$,

or as

$$1 + 4\alpha^2 >=< (1+\alpha^2)^2,$$
$$1 >=< \pm(1-\alpha^2).$$

Taking the minus sign,

$$E_c >=< E_0 \text{ as } \alpha <=> \sqrt{2}.$$

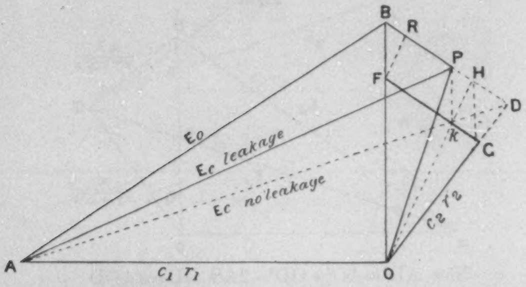
Taking the plus sign,

$$E_c >=< E_0 \text{ as } \alpha >=< 0\,;$$

that is $E_c > E_0$ if $\alpha$ lies between $\sqrt{2}$ and 0, not including these values.

### *Case of an identical Primary and Secondary with Magnetic Leakage.*

Fig. 4.



As before make $OA = C_1 r_1$, $OB = pLC_1$, then $AB = E^0$. Let $M = \beta L = \beta N$.

In OB take a point F such that $OF = \beta \times OB = pMC_1$. Draw OD making angle $\theta =$ angle OAB with OB and drop perpendicular BD. Drop perpendicular FG on OD, then $FG = pNC_2$, and $OG = C_2 r_2$.

Through G draw GH parallel to OB and cutting BD in H. Join OH and let it cut FG in K, through K draw KP parallel to OB and cutting BD in P.

Through F draw FR parallel to OH and meeting BD in R.

Then
$$\frac{BH}{RH} = \frac{OB}{OF} = \frac{1}{\beta}.$$

Therefore $RH = \beta \,.\, BH$, but $BH = FG$, so

$$RH = \beta \,.\, FG = \beta p N C_2 = p M C_2.$$

Again, RH = FK = BP since FR is parallel to OH and KP to OB.

Now OP is the resultant of $OB = pLC_1$, and $BP = pMC_2$. Join AP.

Then AP represents $E_c$.

If there were no leakage AD would represent $E_c$. Now AP is obviously less than AD, or the effect of leakage is to diminish the ratio $\frac{E}{E_0}$, that is the ratio of $\frac{I}{I_1}$.

Obviously from the figure the greater the leakage the lower F, the smaller FG and BH, the smaller also the ratio $\frac{BP}{BH}$, and consequently the nearer P to B, that is the nearer the value of $E_c$ to that of $E_0$.

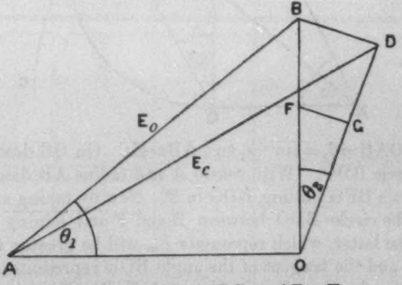
### *Case of Two Coils with different Time-Constants without Magnetic Leakage.*

$$\text{Primary} \quad L, r_1, \text{ and } \alpha_1 = \frac{pL}{r_1}\ ; \ \tan\theta_1 = \alpha_1.$$

$$\text{Secondary } N, r_2, \text{ and } \alpha_2 = \frac{pN}{r_2}\ ; \ \tan\theta_2 = \alpha_2.$$

$$M^2 = LN, \text{ so that } \frac{M}{N} = \frac{L}{M}.$$

Fig. 5.



$$OA = C_1 r_1, \quad OB = pLC_1, \quad AB = E_0.$$

$$\text{Make } \frac{OF}{OB} = \frac{M}{L}. \quad \therefore OF = pMC_1.$$

Draw OD making angle $\theta_2 = \tan^{-1}\alpha_2$ with OB, and drop perpendiculars FG and BD on to OD.

Then $\quad FG = pNC_2$ and $OG = C_2 r_2$.

Now

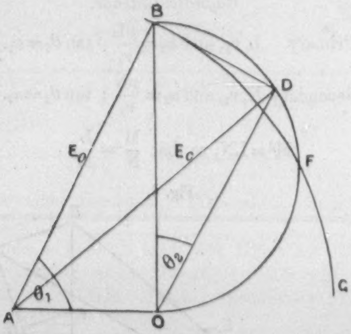
$$\frac{M}{N} = \frac{L}{M} = \frac{OB}{OF} = \frac{BD}{FG} \text{ (by similar triangles).}$$

$$\therefore \ BD = FG \times \frac{M}{N} = pNC_2 \times \frac{M}{N} = pMC_2.$$

Hence OD represents the back E.M.F. in primary due to self and mutual inductions, and $AD = E_c$.

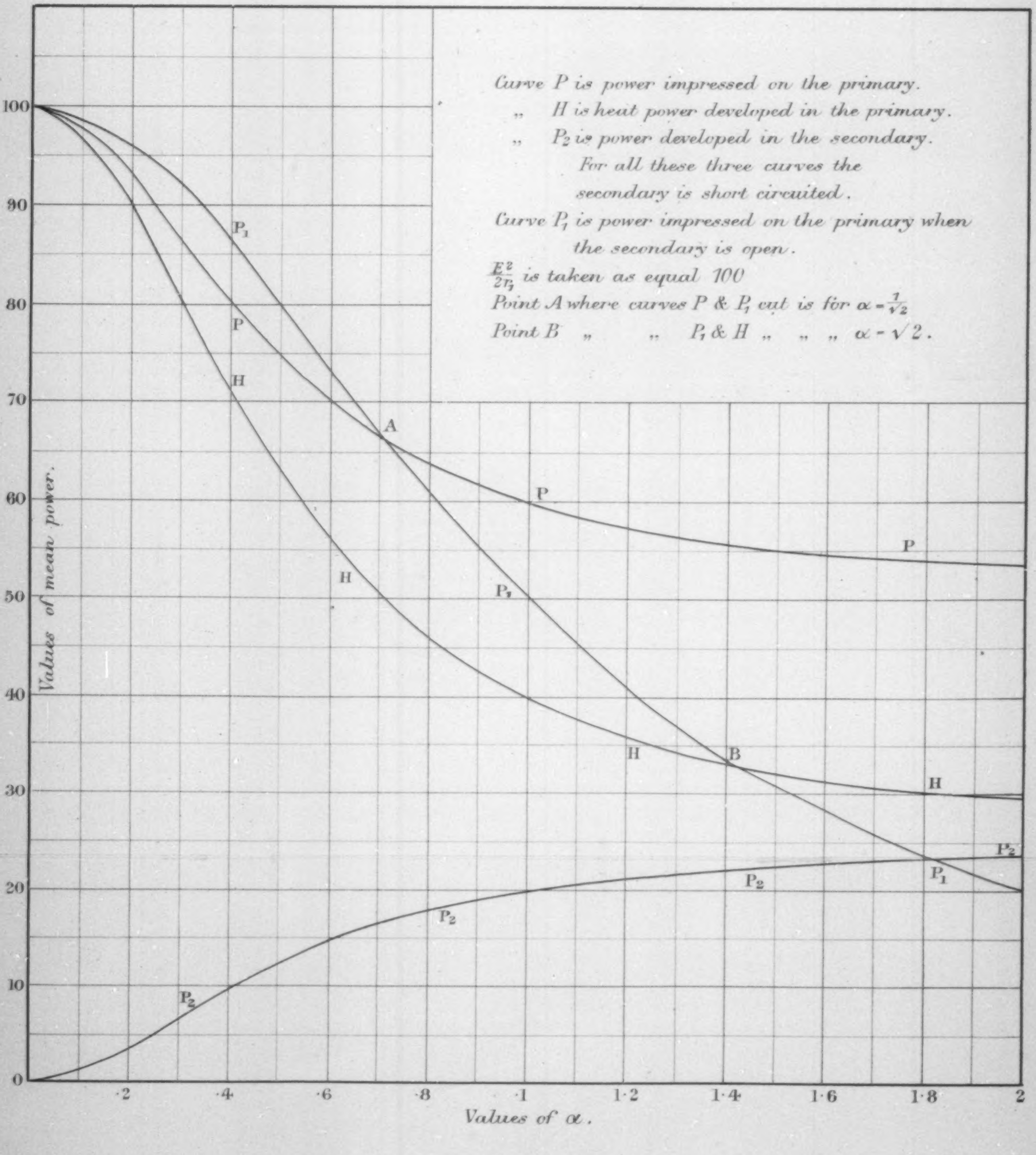
However large the value of $\alpha_1$ (unless it were infinite, which is of course not possible) it is always possible by making $\alpha_2$ sufficiently small to obtain $E_c$ greater than $E_0$. In fig. 6 the

Fig. 6.



angle $OAB = \theta_1 = \tan^{-1}\alpha_1$ and $AB = E_0$. On OB describe the semicircle BDO. With centre A and radius AB describe the the circle BFG cutting BDO in F. Now by taking any point D in the circle BDO between B and F and joining OD and AD, the latter, which represents $E_c$, will be greater than AB or $E_0$, and the tangent of the angle BOD represents $\alpha_2$.

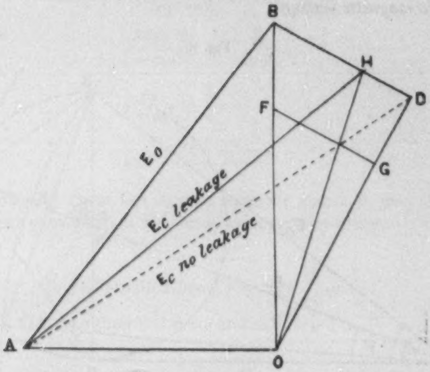
Obviously when D coincides with F, $E_c = E_0$, or closing the secondary makes no difference to the impedance of the primary; while if D be between F and O, $E_c$ is less than $E_0$


Curve P is power impressed on the primary.
„ H is heat power developed in the primary.
„ $P_2$ is power developed in the secondary.
For all these three curves the secondary is short circuited.
Curve $P_1$ is power impressed on the primary when the secondary is open.
$\frac{E^2}{2r_1}$ is taken as equal 100
Point A where curves P & $P_1$ cut is for $\alpha = \frac{1}{\sqrt{2}}$
Point B „ „ $P_1$ & H „ „ „ $\alpha = \sqrt{2}$.

Mintern Bros. lith.

### *Case of Two Coils with different Time-Constants with Magnetic Leakage.*

Fig. 7.



Let $M^2=\beta^2LN$ so that $\frac{M}{N}=\beta^2\frac{L}{M}$.

Construction is the same as in the last case, or $\frac{OF}{OB}=\frac{M}{L}$; H is taken so that $\frac{BH}{BD}=\beta^2$.

Now $\frac{BD}{FG}=\frac{L}{M}$; $\therefore\ \frac{BH}{FG}=\beta^2\frac{L}{M}=\frac{M}{N}$,

so that

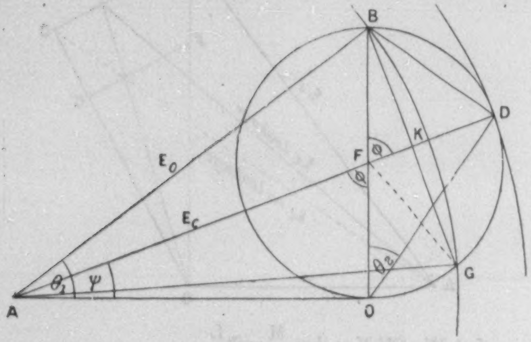
$$BH=\frac{M}{N}\cdot FG=\frac{M}{N}\cdot pNC_2=pMC_2.$$

∴ OH is the back E.M.F in the primary due to self and mutual inductions, and consequently $AH=E_c$.

$AD=E_c$ if there be no leakage.

**Problem I.** *A transformer with a given primary (or $\alpha_1$ known), to find the value of $\alpha_2$ for secondary so as to make $\frac{E_c}{E_0}$ or $\frac{I}{I_1}$ a maximum. Also to find the critical value of $\alpha_2$. No magnetic leakage.*

Fig. 8.



Let $\theta_1 = \tan^{-1} \alpha_1$ which is known.

Draw $OA = C_1 r_1$; draw OB at right angles to OA and equal to $pLC_1$ or $\alpha_1 C_1 r_1$. Then $AB = E_0$ and the angle OAB $= \theta_1$.

On OB as diameter describe the circle ODB with centre F; then $OF = \frac{1}{2}OB$.

Join AF and produce it to cut the circle in D.

Then AD is the greatest straight line that can be drawn from A to cut the circle ODB, since if two circles touch the line through their centres passes through the point of contact

Join BD and OD, then the angle BOD $= \theta_2$ and $\frac{BD}{OD} = \tan \theta_2 =$ the required value of $\alpha_2$.

Let the angle BFD $= \phi$ and the angle OAD $= \psi$.

Then

$$\theta_2 = \tfrac{1}{2}\phi = \tfrac{1}{2}\left(\frac{\pi}{2} - \psi\right) \text{ or } 2\theta_2 = \frac{\pi}{2} - \psi.$$

Now $\frac{\tan\psi}{\tan\theta}=\frac{OF}{OB}=\frac{1}{2}$, or $\cot\psi=\frac{2}{\tan\theta_1}$;

also

$$\tan 2\theta_2=\tan\left(\frac{\pi}{2}-\psi\right)=\cot\psi=\frac{2}{\tan\theta_1}.$$

Hence

$$\frac{2\tan\theta_2}{1-\tan^2\theta_2}=\frac{2}{\tan\theta_1},$$

or

$$\frac{\alpha_2}{1-\alpha_2^2}=\frac{1}{\alpha_1},$$

or

$$\alpha_2=\frac{\sqrt{4+\alpha_1^2}-\alpha_1}{2}.$$

Obviously from the figure, however small $\theta_1$ may be, $\theta_2$ is never greater than 45°, or $\alpha_2$ greater than unity.

*To find the Maximum Value of* $\frac{E_e}{E_0}$ *or* $\frac{I}{I_1}$.

Call $OA=1$, then $OB=\alpha_1$, and $AB=\sqrt{1+\alpha_1^2}$.

Now

$$AD=AF+FD=\sqrt{1+\frac{\alpha_1^2}{4}}+\frac{\alpha_1}{2}=\frac{\sqrt{4+\alpha_1^2}+\alpha_1}{2}.$$

But

$$\frac{E_e}{E_0}=\frac{AD}{AB}=\frac{\sqrt{4+\alpha_1^2}+\alpha_1}{2\sqrt{1+\alpha_1^2}},$$

or the maximum value of $\frac{I}{I_1}=\frac{\sqrt{4+\alpha_1^2}+\alpha_1}{2\sqrt{1+\alpha_1^2}}$.

Hence

$$\left(\frac{I}{I_1}\right)^2_{\text{max.}}=\frac{4+\alpha_1^2+\alpha_1^2+2\alpha_1\sqrt{4+\alpha_1^2}}{4(1+\alpha_1^2)}$$

$$=1+\frac{\alpha_1(\sqrt{4+\alpha_1^2}-\alpha_1)}{2(1+\alpha_1^2)}.$$

Now since $\sqrt{4+\alpha_1^2}$ is always greater than $\alpha_1$, whatever value $\alpha_1$ has (except $\infty$) $\left(\frac{I}{I_1}\right)^2_{\text{max.}}$ is always greater than unity, or $\left(\frac{I}{I_1}\right)_{\text{max.}}$ is always greater than unity.

### *To find the Critical Value for $\alpha_2$.*

With centre A and radius AB describe a circle cutting the circle BDO in G. Then the angle GOB is the critical value of $\theta_2$, and $\tan\theta_2 = \frac{GB}{OG}$ = the critical value of $\alpha_2$.

Join AG and FG. Now AG=AB, FG=FB, and AF is common.

∴ the angle AFG=the angle AFB, and hence the angle GFK=the angle BFK.

But BF=FG, and FK is common.

∴ BK=KG, but BF=OF.

Hence OG is parallel to FK.

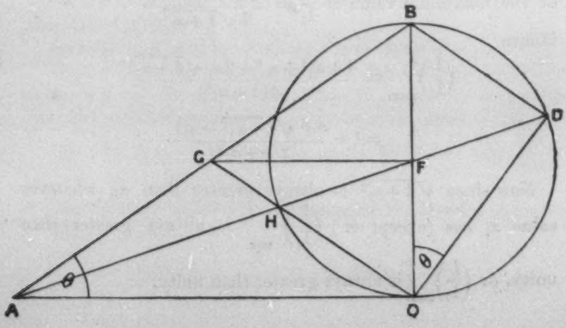
∴ the critical value of $\theta_2$ or the angle GOB=the angle BFD=$\phi$.

But $\phi = 2\theta_2$ for maximum $\frac{I}{I_1}$.

∴ the critical value of $\theta_2$=twice the value of $\theta_2$ that gives $\frac{I}{I_1}$ a maximum.

**Problem II.** *A transformer with primary and secondary having the same time-constants, to find the value of $\alpha$ to give maximum $\frac{I}{I_1}$. No magnetic leakage.*

Fig. 9.



*Construction.* Draw a circle with centre F, and take any diameter OB, draw OA at right angles to OB.

With centre F and radius 3OF describe a circle cutting OA in A.

Join AB and AF and produce AF to meet the circle in D. Join BD and OD.

Then the angle OAB = the angle BOD = $\theta$, and the required value of $\alpha$

$$= \tan\theta = \frac{OB}{OA} = \frac{BD}{OD}$$

*Proof.* Call the angle BOD = $\theta$.

Join OH and produce it to meet AB in G: join FG.

Now AH = HD by construction, and OH is parallel to BD.

Hence GH is parallel to BD, and therefore AG = GB.

Again, since AG = GB, and OF = FB, GF is parallel to OA.

$\therefore$ the angle BFG = the angle BOA = a right angle.

Now OF = FB and FG is common: hence

$$OG = GB = AG.$$

$\therefore$ the angle $GAO = GOA = \frac{\pi}{2} - GOB = BOD = \theta$, since the angle HOD being in a semicircle $= \frac{\pi}{2}$.

$\therefore$ the angle $BAO = BOD = \theta = \tan^{-1}\alpha$, or the coils have the same time-constant.

Now from the solution of Problem I. the construction is such as to give a maximum value for $\frac{I}{I_1}$, but it is so arranged that while giving a maximum $\frac{I}{I_1}$ the time-constant of the secondary is the same as that of the primary. Q.E.F.

*To find $\alpha$ or* $\tan\theta$.

$$AF = 3OF \text{ (by construction).}$$

Now $AO^2 = AF^2 - OF^2 = 8OF^2$.

$$\therefore AO = 2OF\sqrt{2}.$$

Now $OB = 2OF$ and $\alpha = \tan\theta = \frac{OB}{OA} = \frac{2OF}{2OF\sqrt{2}} = \frac{1}{\sqrt{2}}$.

*To find the maximum value of* $\frac{I}{I_1}$, *that is of* $\frac{E_e}{E_0}$.

$$AO^2=8OF^2 \text{ and } AD=4OF.$$

Now

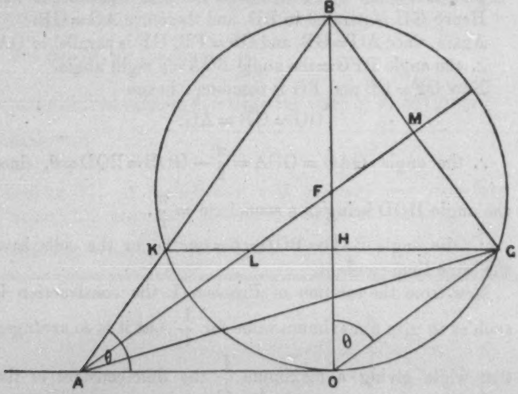
$$AB=\sqrt{AO^2+OB^2}=\sqrt{8OF^2+4OF^2}=\sqrt{12OF^2}=2OF\sqrt{3}.$$

Also

$$\frac{I}{I_1}=\frac{E_e}{E_0}=\frac{AD}{AB}=\frac{4OF}{2OF\sqrt{3}}=\frac{2}{\sqrt{3}}=1{\cdot}155.$$

**Problem III.** *A transformer with primary and secondary having the same time-constants, to find the critical value of $\alpha$. No magnetic leakage.*

Fig. 10.



*Construction.* Draw any circle with centre F and a diameter OB, draw OA at right angles to OB. In OB take a point H such that BH=2OH or $OH=\frac{1}{3}OB$.

Through H draw KHG parallel to OA and meeting the circle in K and G.

Join BK and produce it to meet OA in A. Join OG and BG.

Then the angle OAB=the angle BOG=$\theta$=the critical angle required, and the critical value of $\alpha=\tan\theta=\frac{OB}{OA}$.

*Proof.* Firstly, to prove the angles OAB and BOG to be equal.

Since KG is parallel to OA, the angles KHB and GHB are right angles, and KH=HG, also BH is common.

Therefore the angle KBH=GBH.

But AOB is a right angle by construction, and BGO because it is in a semicircle.

Hence the angle BAO=BOG=$\theta$.

Secondly, to prove that AG=AB or $E_c=E_0$, in which case from Problem I. it is known that $\theta$ is the critical angle. Join AF and produce it to meet BG in M.

Since KG is parallel to AO by construction,

$$\frac{FH}{FO}=\frac{LH}{AO};$$

but $FH=\frac{1}{3}FO$ (since $OH=\frac{1}{3}OB=\frac{2}{3}FO$);

$\therefore$ $LH=\frac{1}{3}AO$.

Again, $\frac{AO}{KH}=\frac{OB}{HB}=\frac{3}{2}$; hence $AO=\frac{3}{2}KH$;

$\therefore$ $LH=\frac{1}{2}KH=\frac{1}{2}HG$ or $LG=3LH$.

But $AO=3LH$; $\therefore$ $AO=LG$;

or AL is parallel to OG; and the angle AMB=AMG=a right angle.

Also BM=MG and AM is common.

$\therefore$ AB=AG or $E_c=E_0$.

### *To find the Critical Value of $\alpha$ or* tan $\theta$.

Since AF is parallel to OG the angle BFM=$\theta$;

$\therefore$ the angle LFH=$\theta$=angle BKH.

Hence $$\frac{LH}{FH}=\frac{BH}{KH}$$

Now $KH=2LH$;

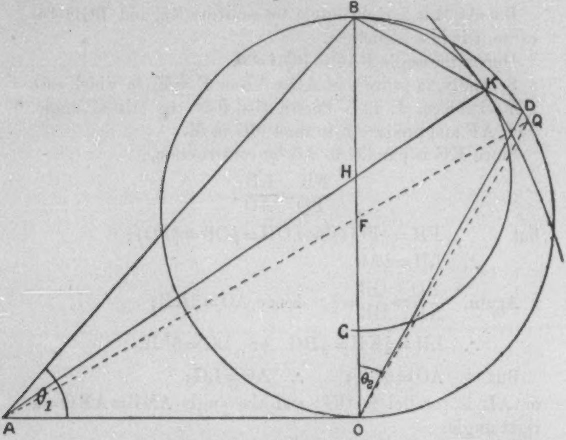
$$\therefore\quad 2LH^2=FH\,.\,BH=\frac{OF}{3}\cdot\frac{4OF}{3}=\frac{4OF^2}{9},$$

or $$LH=\frac{OF\sqrt{2}}{3}.$$

Now $$\alpha=\tan\theta=\frac{LH}{FH}=\frac{OF\sqrt{2}}{3FH}=\frac{OF\sqrt{2}}{3\,.\,\frac{OF}{3}}=\sqrt{2}.$$

PROBLEM IV. *A primary with given time-constant, or* $\alpha_1$ *known, magnetic leakage or* $\beta$ *known, to find the value of* $\alpha_2$ *so as to make* $\frac{I}{I_1}$ *a maximum.*

Fig. 11.



*Construction.* Draw a circle BDO with diameter OB and centre F; draw OA at right angles to OB and make OA of such length that $\frac{OB}{OA}=\alpha_1$.

Join AB. Then the angle OAB represents $\theta_1$.

From B mark off BH such that

$$\frac{BH}{BF}=\beta^2 \quad (M=\beta\sqrt{LN}).$$

With centre H and radius HB describe circle BKG.

Join AH and produce it to cut circle BKG in K.

Join BK and produce it to cut circle BDO in D.

Join OD, then the angle BOD is the required value of $\theta_2$, and tan BOD$=\frac{BD}{OD}$ the required value of $\alpha_2$.

Also $\frac{AK}{AB}$ is the maximum value of $\frac{E}{E_0}$ or of $\frac{I}{I_1}$.

*Proof.* Since BH$=\beta^2$BF, BG$=\beta^2$BO, and BK$=\beta^2$BD (for join KG, then KG is parallel to DO since the angles at

K and D are both right angles, being in semicircles, and therefore by similar triangles $\frac{BK}{BD}=\frac{BG}{BO}$).

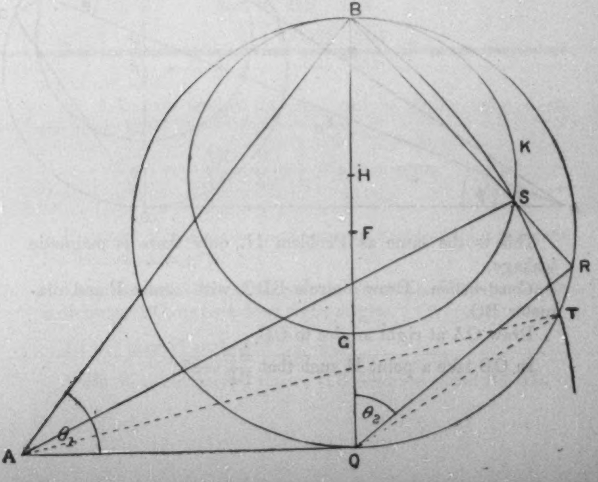
It follows then that, whatever the value of $\theta_1$ the point K lies on the circle BKG when BK represents the back E.M.F. in the primary due to mutual induction, OK the resultant back E.M.F. due to mutual and self-induction, and AK=$E_e$ the impressed potential difference.

With centre A describe a circle touching the circle BKG, then K is the point of contact, since AK passes through H the centre of circle BKG. Therefore AK is the maximum value of $E_e$, and the angle BOD the value of $\theta_2$, which gives this maximum value for $E_e$. If there were no leakage the dotted line AQ would represent the maximum value of $E_e$, and the angle BOQ the corresponding value of $\theta_2$.

It is easily seen from the figure that the effect of leakage is to diminish the maximum value of $\frac{E_e}{E_0}$ or of $\frac{I}{I_1}$, and to diminish also the value of $\theta_2$, and consequently that of $\alpha_2$, necessary to obtain it.

PROBLEM V. *Same conditions as Problem* IV.; *to obtain the critical value of* $\alpha_2$.

Fig. 12.



The first part of the construction is the same as in Problem IV.

With centre A and radius AB describe circle BST cutting circles BKG and BTO in S and T respectively. Join BS.

Produce BS to meet circle BTO in R and join OR.

Then the angle BOR is the critical value of $\theta_2$, and that of $\alpha_2$

$$=\tan\theta_2=\frac{BR}{OR}.$$

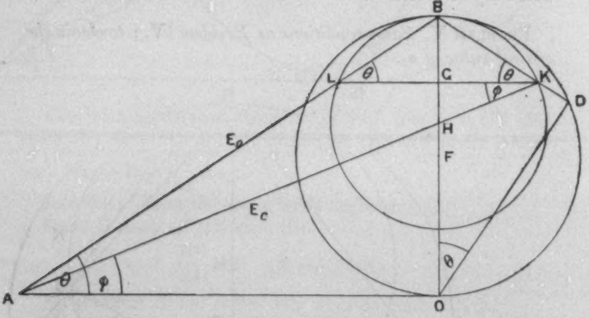
If there were no leakage the angle BOT would be the critical value of $\theta_2$.

The proof is obvious from that of Problem IV.

Here, again, the effect of magnetic leakage is to diminish the critical value of $\theta_2$, and consequently that of $\alpha_2$.

PROBLEM VI. *A transformer with primary and secondary having the same time-constants, to find the value of $\alpha$ to obtain $\frac{I}{I_1}$ a maximum, the magnetic leakage or value of $\beta$ being known.*

Fig. 13.



This is the same as Problem II., only there is magnetic leakage.

*Construction.* Draw a circle BDO with centre F and diameter BO.

Draw OA at right angles to OB.

In OB take a point H such that $\frac{BH}{BF}=\beta^2$.

Take a point G in BH such that $\frac{HG}{GB}=\frac{OH}{OB}$.

(For method of obtaining G geometrically see Problem VII.)

With centre H and radius HB describe circle LBK.

Through G draw LGK parallel to OA and meeting the circle LBK in L and K.

Join BL and produce it to meet OA in A.

Join BK and produce it to meet circle BDO in D. Join OD and AK.

Then $\frac{AK}{AB}$ is the maximum value of $\frac{I}{I_1}$; and the angle

$$BAO=BOD=\theta \text{ is the required angle;}$$

and

$$\tan\theta=\frac{OB}{OA} \text{ is the required value of } \alpha.$$

*Proof.* Obviously the angle LBG = the angle KBG.

$\therefore$ the angle BAO = the angle BOD = $\theta$.

Call H the point where AK cuts OB.

Now since LK is parallel to OA, the angle BAO = the angle BLK = BKL = $\theta$; and the angle KAO = LKA = $\phi$ say.

Now

$$\frac{\tan\phi}{\tan\theta}=\frac{OH}{OB}=\frac{HG}{GB}.$$

But by construction, when $\frac{OH}{OB}=\frac{HG}{GB}$, H is the centre of the circle LBK.

$\therefore$ AK is the longest line that can be drawn from A to the circle LBK.

$$\therefore \quad \frac{AK}{AB}=\frac{E_c}{E_0}=\frac{I}{I_1} \text{ is a maximum.}$$

PROBLEM VII.—*Same conditions as Problem* VI.; *to obtain the critical value of* $\alpha$.

*Construction.* Draw with centre F a circle BDO and take a diameter BO, draw OA at right angles.

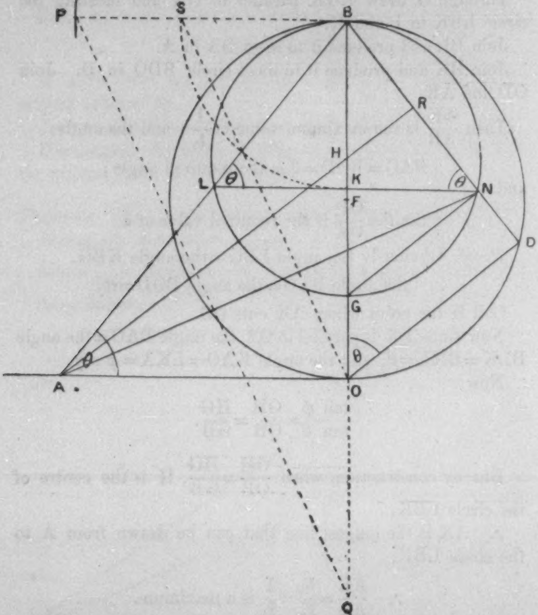
In BO take H such that $\frac{BH}{BF}=\beta^2$.

With H as centre and radius HB describe circle BNGL.

In GB take a point K such that $\frac{GK}{KB}=\frac{OH}{OB}$.

(To obtain K, produce BO to Q making OQ=OH, draw

Fig. 14.



BP=BG, join PQ, and through O draw OS parallel to PQ, then BK=BS.)

Through K draw LKN parallel to OA and meeting circle BNGL in L and N.

Join BL and produce to meet OA in A.

Join BN and produce to meet circle BDO in D. Join OD and AN.

Then the angle BAO=BOD=$\theta$, and

$$AN=AB \quad \text{or} \quad E_e=E_0 \quad \text{or} \quad I=I_1.$$

*Proof.* Obviously the angle BAO = BOD as before. Join AH and produce it to meet BD in R. Join GN. Now

$$\frac{GK}{KB}=\frac{\tan GNK}{\tan KNB};$$

but

$$KNB=BLK=BAO=\theta.$$

Again,

$$\frac{OH}{OB}=\frac{\tan OAH}{\tan BAO};$$

but $\frac{GK}{KB}=\frac{OH}{OB}$ by construction.

$$\therefore \quad \frac{\tan OAH}{\tan\theta}=\frac{\tan GNK}{\tan\theta};$$

∴ the angle GNK = the angle OAH, or AR is parallel to GN;

∴ the angles at R are right angles and BR = RN.

Also AR is common.

∴ AB = AN or $E_c = E_0$.

In all the above geometrical constructions the phase-angle between the secondary and primary currents is represented by $\frac{\pi}{2}+\theta_2$, or, when the primary and secondary have the same time-constant, by $\frac{\pi}{2}+\theta$.

## Discussion.

Prof. **Minchin** showed that the impedances might be represented by two hyperbolas, having $p$ as abscissæ and the squares of the impedance as ordinates. These could be readily constructed from the data given. A line representing the primary inductance, drawn on the same diagram, intersects one hyperbola, showing that the impedance has always a maximum value. By a simple construction the phase-angle between the primary and secondary currents could be determined for any given conditions.

Dr. **Sumpner** observed that increased impedance on closing the secondary necessarily meant a decrease in the lag of the primary current behind the primary P.D.

Mr. **Blakesley** was pleased to see the geometrical method of such service, and thought it much simpler than the analytical one. The reason why increased impedance on closing the secondary of ordinary transformers had not been noticed, was because their lag-angles were very large. In a figure published some years ago to represent the actions of transformers, the angles he had chosen were such as would make the primary impedance increase on closing the secondary. Giving an expression connecting the primary currents on open and closed secondary respectively, he now showed that to get increased impedance the sum of the lag-angles in primary and secondary must exceed 90°. To get large power in the secondary, the primary lag should be nearly 90° and the secondary about 45°. He also pointed out that some of the figures in the paper might be simplified considerably.

Prof. **Perry** said he had long had the impression that if a sufficiently small current were taken from the secondary, increased impedance would be observable in all cases, and he quoted some numbers he had given in the Phil. Mag. for 1891, showing a decided increase.

Mr. **Rimington**, in reply, said he was not aware that the effect he had now brought forward had been observed previously. The result was completely worked out analytically before using geometrical methods.

## II. *A New Mode of making Magic Mirrors.*

### *By* J. W. Kearton[*].

THE first explanation that occurred to me on seeing the Japanese mirror about fourteen months ago was that the face might bear directly invisible differences in polish, which a powerful beam of light would probably convert into visible ones by reflexion on to the screen. To produce such minute differences, it was my intention to take pairs of different metals closely agreeing in colour and reflective power, as silver and platinum, and to deposit electrically in the form of some easily recognizable figure a thin coating of the one metal on a groundwork of the other. Very faint mercuric staining of bright metallic surfaces was also contemplated. These ideas, however, resolved themselves into a test much simpler, yet involving the same principle. A piece of metal was so polished that in subdued daylight a cross, more finely burnished than the general surface of the plate, could just be distinguished. Reflected on to the screen, the figure came out exceedingly faint; and this fact, apart from the consideration that figures so produced could have only a precarious existence, was sufficient to condemn the hypothesis in question.

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[*] Read January 26, 1894.

This result has a bearing upon another hypothesis—one worthy of prompt burial with the quiddities and essences of the purely deductive method, viz., that the magic-mirror phenomena are due to local molecular rearrangements in the reflecting surface, brought about by unequal cooling of the mass of the mirror. Now, since it is held that the regularity or convexity of the surface is not thereby affected, this molecular rearrangement can put itself in evidence optically only by reflecting more or less light than the parts of the surface unaffected by irregular cooling. But it has been shown that with figures so pronounced as to be directly visible, the electric beam is powerless to produce results comparable in intensity with those given by the Japanese mirror; much less will directly invisible figures of the type under reference come up to the required standard.

The plate used in the foregoing experiment, whilst furnishing no clue in virtue of its polished figure, yet presented evidence that pointed clearly in the direction where a solution of the problem was to be found. Strikingly well-defined lines and dapplings of light were thrown on the screen by light reflected from the disk. These marks were found to correspond to concave strains produced by hammering the plate into rough convexity before scouring down with charcoal. Depressions produced by electro-deposition of silver on a silvered plate, protected in parts by varnish according to the figure desired, were therefore tried; but they invariably deepened into the underlying brass before the sharp edges of the figure were polished away.

Next, a fairly thick coating of silver was deposited on the plate, and a pointed bit of agate was repeatedly drawn with pressure over certain parts of the porous layer of metal. The figures thus obtained were startling; for the depressions appeared on the screen as reticulated lines of deep shade, which had their analogue in the broken spinal divisions left by the agate point. The bad working of metals electrically deposited caused me to give up the deposition method.

My plate of brass was next slung up in a weak solution of copper sulphate and sulphuric acid on the positive wire of a pint bichromate-cell. After an immersion of four minutes, the parts of the plate not protected by the naphthaline solution of sealing-wax came out beautifully fretted. After several attempts on these lines, and two days after the lecture delivered here by Prof. S. P. Thompson on the 27th of January last on the Magic Mirror, my first success was achieved in the shape of a mirror 2 inches in diameter, representing a stem with leaves and a guide-post standing in a mound of earth. From that mirror to my present one, the first of the new class being completed in the following July, was, however, a far cry. Applied to larger mirrors and figures, the electrical method proved essentially bad. Exactly contrary to what was required, the figures were deeper at the edges of the lines than at the central parts: indeed, a broad line scoured down into two lines defining the lateral limits of the original one.

Nitric acid was finally adopted as the figure-eating agent, care being taken to use good brass and to polish well before immersion, so that the action on the plate might be uniform. Smooth figures were thus produced after immersions of upwards of six seconds in strong acid. The walls of the figures are perpendicular to the surface of the disk, and the determination of their proper height relatively to the breadth of the lines of the figure involved much further labour. The process of scouring with Sheffield lime and swans'-down calico has a double effect—it rounds off the upper rectangular edges of the walls, and at the same time converts the flat floors of the figure into concave depressions, the walls and floors finally merging into one concave sweep. This curve, with narrow lines, is sharper than with broad lines; consequently the latter may disappear, while the former remain visible. Very brief immersions in the acid are therefore not suitable for figures having lines differing much in breadth. Long immersions, on the other hand, are objectionable both on the ground of the excessive labour in rounding off the edges, and of the well-nigh impossible task of reducing uniformly the deep runnels of the figure by scouring the general surface with charcoal.

Gradations in depth according to the breadth of the several limbs were therefore tried, and produced in the following way:—The figure, say of a tree, is made by removing paraffin wax from the brass plate with a pointed stick of boxwood, and is then fixed by a very short immersion in the acid. The slender branches are now painted over with hot wax, and the broader branches and trunk are reduced in breadth symmetrically by the same means, the plate then being immersed a second time. By a repetition of alternate painting and immersing, all the members of the figure are made to increase in depth by fine gradations from the boundary lines to the central parts. This method, specially applicable to figures with very broad and narrow lines, is, however, rather troublesome, and does not give satisfactory results unless the gradations are minute, which otherwise will be brought out by reflexion on to the screen.

Reverting to single immersions, final experiments were made with plates bearing figures prepared in the usual way, viz. by removal of wax, a record being kept of the strength of the acid and the time of immersion in each case. The result is that for figures with lines ranging from $\frac{1}{16}$ to $\frac{3}{8}$ of an inch in breadth, an immersion of 3 seconds in a solution of 5 volumes of concentrated nitric acid to 2 of water gives a satisfactory depth.

The next step was to produce figures in low relief, which come out on the screen in shade. As there is in this case no intersection of the reflected rays, and, consequently, no blotting out or dimming of the figures, very narrow lines may be used. These are conveniently drawn with a camel's-hair brush and sealing-wax dissolved in naphtha. From 1 to 2 seconds' immersion, according to the breadth of the characters, will be found sufficient.

## Discussion.

Prof. S. P. Thompson said the chief interest of Mr. Kearton's work was that he had succeeded in producing mirrors by a process which Prof. Ayrton had found unsuccessful. The spherical polisher used by Mr. Kearton might have something to do with the result obtained. Some of the mirrors had been gilt after polishing and the reflected pattern improved thereby.

Prof. Ayrton said he was greatly interested to see that mirrors could be produced by the chemical method. The polisher used by the Japanese was the flat end of a tight bundle of special straw cut crosswise. When the true explanation of the magic properties was found out, the chemical method was not pursued further.

The Rev. F. J. Smith mentioned that he had produced magic properties on silvered glass by the inductoscript method. Although no markings could be seen directly, the pattern showed itself when light was reflected from the surface to a screen.

## III. *Some Observations on Diffraction.*

*By* W. B. Croft, *M.A.*[*]

[Plates III.-VI.]

It is proposed to illustrate various forms of this phenomenon by photographs[†] produced directly from the wave-interference.

After the inauguration of the idea about 1665 by Grimaldi, Hooke, and Huygens, there was little progress, either in extended observation or in philosophical grasp of the principles, until the beginning of this century. Since that time the subject has been treated in two ways.

### 1st. *The Diffraction of* Fraunhofer *and* Schwerd.

This kind is familiar to many through the observations of Sir John Herschel of Diffraction in a Telescope. It is sometimes described as the Diffraction from Parallel Light.

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[*] Read January 26, 1894.

[†] It is not convenient to reproduce all the photographs: the selected figures 2, 3, 4, 10 12 13, 71 72, 75, 83 will be found on Plates III.-VI.

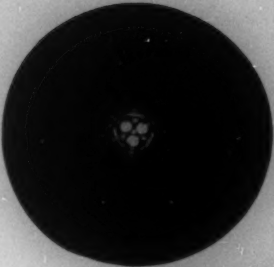

Fig. 2.

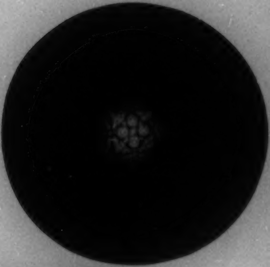

Fig. 3

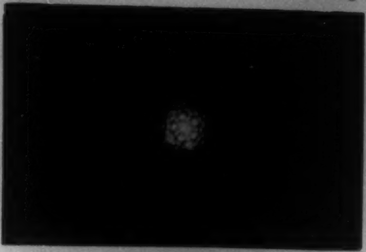

Fig. 4.

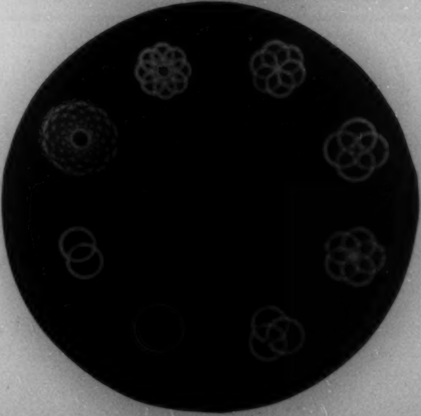

Fig. 10.

Although more often named after Fraunhofer, as is due to the first great worker in this direction, high tribute is always paid to the more perfect consummation of theory and experiment which was published by Schwerd of Spires in 1835.

A telescope is focussed to a star or a distant point of light, and various limiting apertures are placed on the outer side of the object-glass. Consider, first, the case of two or three narrow parallel lines of light: they constitute an elementary grating, and light from the star passing from them to the object-glass will come as if from several stars lying on either side of the real star, all being spectral images except the central one. The object-glass focusses these at the usual place, then the eyepiece magnifies them and transmits parallel rays of light; so there is a broken line of light across the field, consisting of the plain image at the centre and the spectra of the successive orders on either side. More complex limiting apertures give these radial groups of images of the source of light, of which the number and direction are regulated by the general form of the aperture: thus a triangle will give three lines across the field or a six-rayed star, a square will give a four-rayed star; a circle concentric with the object-glass, however, will give concentric circular spectra.

The objects whose effects have been photographed consist of combinations of thin circular lines of light on a dark glass plate $\frac{3}{4}$ inch diameter; this fits into a cap at the end of a telescope, and each figure in turn is brought to a small opening in front of the centre of the object-glass: this is known as Bridge's apparatus, constructed some years back for this form of diffraction. Fig. 8 almost represents these figures; it has slight traces of diffraction of the other kind. Figs. 1–7 (figs. 2, 3, 4 on Pl. III.) represent the Fraunhofer diffraction of the seven more complex figures: the simplest figure, which consists of two concentric circles, gives concentric spectra by both methods of observation.

### 2nd. *The Diffraction in Shadows*: Fresnel's *Diffraction.*

This is described by Lord Rayleigh as the Diffraction when the source of light is not in focus, or in Jamin's *Cours de Physique* as Diffraction from a Spherical Wave. Light is condensed on a minute pinhole in a thin metal plate; about a foot from this the diffracting object is placed, and at a similar distance beyond a microscope eyepiece receives the shadows: they may be observed with the eye or projected on the screen of a camera for photography. The rays emerge from the eyepiece parallel, and give an image on the screen which varies in size but not in quality as the screen is moved; infinite changes, however, are made by variations in the relative distances of the source of light, object, and lens or eyepiece.

In order to consider a fundamental principle of importance, take at first more simple apparatus, a convex lens instead of the Huygens eyepiece, and let the object, which is the glass plate with circle combinations, be illuminated with parallel uncondensed sunlight. If the lens is placed at its focal distance from the object, rays emerge parallel and make simple images of circles without any diffraction developments; they are always in focus wherever the screen is placed, and are naturally greater when it is more distant. If the lens is slightly moved from this position in either direction, the emerging rays cross one another and produce interference developments. The figures made when the lens is moved towards the object are inferior in definiteness.

A wave impinging on an edge gives rise to the secondary waves of Huygens, and from each new centre waves spread out in all directions, although the incident light may have a plane front or be a parallel pencil; but a pencil, after emerging parallel from a lens, cannot be considered to have rays striking out obliquely so as to interfere. From this may be imagined the formation of diffraction-rings in a telescope directed to a star when the eyepiece is moved so that the image made by the field-glass is out of its focus; the image is nearly a point of light; while the rays emerged from the eyepiece parallel they would not interfere, but directly they cross one another on emergence they give rise to systems of concentric rings. This phenomenon may be well seen by looking through the eyelashes towards a distant lamp while a fine rain is falling: minute spheres of water fall upon the eyelashes; these short-focus lenses make images of the lamp in front of the eye, and the lens of the eye cannot focus or turn parallel the rays from these points; for a moment a number of fine concentric rings

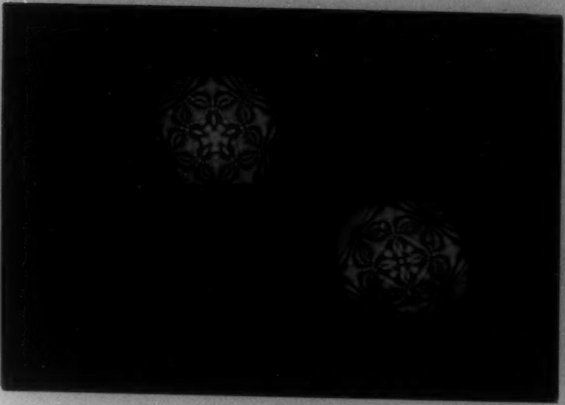

Fig. 12.

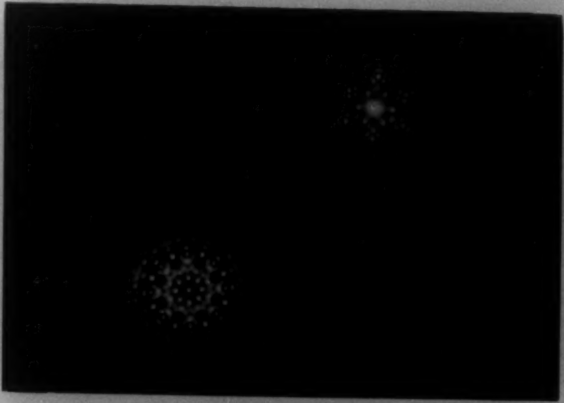

Fig. 13.

may be seen, which are constantly evanescent and constantly renewed by fresh-falling specks of water.

There is another phenomenon sometimes revealed when a divergent pencil from a short-focus lens or spherical reflecting surface falls upon the eye in such a way that the eye cannot focus it: a small illuminated disk is seen with fine ramified lines from the centre; in this the eye sees its own blood-vessels: this is easily seen by holding a pinhole near to the eye.

Abundant examples of diffraction may be observed without any apparatus: a distant lamp viewed through the eyelashes on a dry evening appears with many spectral images made by this simple grating: an umbrella can be seen in the same way to act as a rectangular grating. If the eyelids are adjusted to the lamplight, 8 or 10 horizontal exterior bands will easily be produced. Most plate-glass windows have become gratings through the scratching by repeated cleaning.

To return to the main experiment. Stronger effects are produced, of course, when sunlight is condensed on to the pinhole, and in this case the position of the convex lens for giving parallel rays on emergence, or for giving the plain image of the object without diffraction, is not exactly its focal distance from the object, for the divergence of the incident rays has some influence; but there always is such a position. Moreover, the elementary experiment cannot be made with the Huygens eyepiece which is now used, for it has not an external focus. Fig. 8 shows the result of placing the object close up to the eyepiece; the beginnings of diffraction may be seen. Fig. 10 (Pl. III.) shows further developments when the distance is increased, and figs. 9, 11, and 12, 13 (Pl. IV.) give the best effects I have at present been able to produce. In these and in most of the other figures a magnifying-glass is necessary to reveal all the fine detail made by the crossing waves in the shadows. It is clear that if the object is capable of giving spectra passing out with much obliquity, they can never come into the field of the eyepiece by this method of observation; and the eyepiece can never focus them, as it does in the Fraunhofer method, in which case the field-glass brings them to the focus of the eyepiece.

It may be said that the Fraunhofer diffraction gives numerous images of the source of light set in radiating forms which depend on the shape of the object, while that of Fresnel commonly gives the main shape of the object embellished with fine detail in the spaces between its various parts, and sometimes curiously inverted in its leading features.

A simpler form of this arrangement demonstrates a leading idea in wave theory : parallel sunlight falls upon a convex lens, while the diffracting object is between this and the screen of the camera, which has no lens. Fair diffraction-effects are made when the object lies in the converging rays, and they are better when it is moved to the divergent pencil, but when it is at the focus the plain original figure is reproduced. At the focus the several rays that started from one point of the sun have again all reunited ; so that in passing the object, although there are many separate rays, there are no two rays which came from the same original point ; and it is only such as these which can produce interference. Here may be seen, in a certain sense, an object and real image on the same side of a convex lens.

### *Diffraction in a Microscope.*

Some notice of this important part of the subject is necessary, although it may not be supported by much illustration or experiment.

It is well, first of all, to be clear as to compound pencils of light which are more or less on the same axes. In a straight line lie A, B, C, D, E, a candle, a device in wire, a convex lens, the images of the candle and the wire : here are two pencils much intermingled : A is in focus at D, but the light here is also impregnated with the shadows of B, which are indefinite and unfocussed, covering a larger area than when focussed at E ; and at this point there is also the indefinite unfocussed light of A.

Very often the object on the stage of a microscope diffuses the illumination and becomes a new source of light, and there is no need to consider pencils from the original source of light. But here we will take the case of a microscope with a diffraction-grating on the stage and a small opening in the diaphragm below. Light passes on to the objective from the grating as if from several small apertures ranged side by side, in pairs of corresponding spectra on either side of the central point, which is white. The objective makes images of these just above itself, and one image of the grating farther on at the top of the tube. If the eyepiece is removed, the eye is able to focus the rays diverging from these images and to see them clearly. But the eyepiece when in its place could not focus such diverging pencils: their light spreads out and fills the field of the eyepiece with general illumination. The visibility of the detail of a finely divided object depends upon shadows thrown by oblique rays. In the case of a grating these oblique rays are so definitely arranged that they go either to the first, second, or higher spectra, and to nothing between. The central pencil comes through the grating normally in parallel rays, and carries with it no appreciable impression of the detail; experiment shows that on placing a stop above the object-glass to cut off the spectral images, the lines of the grating can no longer be seen, although there is still good illumination. Now the first lot of oblique rays, while on their way from the grating to its focus in the eyepiece, take their course through the first spectra; but they are unfocussed as regards the grating at that position just above the objective, covering a larger area than the spectra. In theory perhaps it is conceivable that by stopping out the spectra alone, and not this larger area, there might be a balance of rays which would betray the shadows at the eyepiece. In practice, however, the first spectra are necessary, and perhaps often sufficient, to show the detail: sometimes the higher spectra may be needed to add breadth to the shadows. In fact, from ordinary objects rays of all degrees of obliquity are available to mark the shadows, but from objects capable of diffraction there is no degree of obliquity less than that which tends towards the first spectrum, and the aperture of the objective must not be too narrow to receive these rays.

The question naturally arises, how far it is possible to know whether an image is a reproduction of the general form of the original object or a diffraction modification: so far as my experience goes, the two appearances may be distinguished. Of course in perfect theory, even if an image could be saved from spherical and chromatic aberration, it must suffer something from the waves: the image of a star in a telescope must be enlarged on this account; but there is a great difference between this falsification and that which arises when the eyepiece is taken out of focus. Fig. 82 is a species of the diatom *Triceratium favus*: it appears as a spotted framework of ill-defined outlines with little groups in the spaces; but the microscope can be adjusted so as to show a well-defined honeycomb with clear hexagonal spaces. In an experiment described above, figures known to be circles are reproduced in their own true form when at one position with regard to a convex lens, and more elaborate ill-focussed forms at positions on either side of the former: it is reasonable, then, to apply this test to distinguish between several images of an unknown original. No doubt the simpler form, which is taken to be the true one, might often be resolved into something more complex by a stronger objective, but this one in its new conditions would again be simple and well-defined amidst its possible diffraction derivatives.

I have not sufficient familiarity with the use of the highest microscope powers, and can imagine that the foregoing tests are not easy, if indeed possible, to apply in such cases; but I suppose that with ¼-inch and lower powers there is no need for uncertainty as to the practical form of the original object.

### Fresnel's *Diffraction from Geometrical Figures.*

Some interesting details can be observed from the shadows about other figures of Bridge's series. It may be here noted that such objects may be made by drawing rather thick figures in ink upon a card about 1 foot square and reducing by photography to 1 inch square: the negatives so produced give the desired transparent lines on a dark ground: it will be understood that a circle means a circular line of light in distinction to a circular area. The play of light-waves in a shadow gives rise to infinite paradox. The most notorious is Arago's bright spot at the centre of the shadow of a circular disk, with which he astonished Napoleon Buonaparte: squares and triangles turn about and point inwards: needles seem to be split down with the light and the two parts point outwards, the thinner needle having the broader central cleft: lastly, lines inclined to one another have the effect of resolving one another into transverse flakes.

Simple figures may be drawn to give a partial explanation of these curious results.

Fig. *a*.

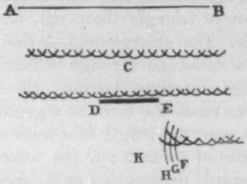

Fig. *a* illustrates the ordinary principle of Huygens, that a wave-front, AB, goes on as a similar wave-front, C, if it be supposed that each point gives rise to a secondary wave: when this strikes upon an obstacle, DE, the waves at the edge, being isolated and not supported by similar waves on the one side, may pass forward so that in directions F, G, H one is always $\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$ of a wave-length in front of the other, causing interference or darkness: these are the exterior shadows: also there can be imagined the action of waves from D and E about a position K which gives the interior bands.

Fig. *b*.

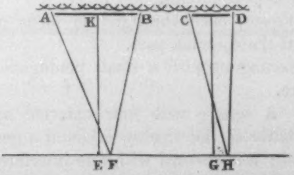

Fig. *b* shows that waves from A and B must always reach E in the same phase, so at the centre there is always light; at F, if the difference of AF and BF $= \frac{\lambda}{2}$, there will be darkness. Now if CH and DH are more nearly parallel than AF and BF are, then, in order to have $CH - DH = \frac{\lambda}{2}$, the point H must be farther from G than F was from E, so the smaller obstacle CD gives the larger bright centre to its shadow. This principle has many consequences: the thinner needle has the broader bright central line, or as a needle is narrowing towards its point the central line will be opening out: at the corner of a square or triangle there will be wedges of light pointing inwards. The enlargement of the image of a star at the focus of a telescope through diffraction is less in a telescope of large aperture, because the waves from the borders of the lens reach the focus at a greater inclination to one another. Again, the length of a wave of yellow light is about 24 millionths of an inch; if the waves from A and B move straight towards one another at K, then the diameter of the bright spot here will be something less than ·000024 inch, too small to be seen, from which it appears that the condition for making visible these phenomena which are connected with such minute quantities is that AF, BF must be nearly parallel: the object must be narrow, or the screen for receiving the shadow must be distant.

The following notes describe the original figures from which the photographs are the shadows:—

14. A circle with four triangular areas.

15. A circular area with four inscribed dark circles.

16. Four circles touching one another; the lines of the circles are gradually made thinner towards the inner part, but they are complete circles.

19. Two ellipses, each through the focus of the other: Arago's spot at the common part.

20. Three pentagons with a small pentagonal area at the common centre.

24 and 29. A square with four external squares at the corners: the latter is the shadow taken at a greater distance from the object; it is covered with fine interference detail.

25 and 28. A square with inscribed square and diagonals.

23, 26, 27, 30. Right-angled triangles put together in sets of four at an acute angle: the detail contains a number of round spots.

31, 39, 40. A chessboard in various states: here again systems of spots are developed.

33. Rows of equilateral triangles, set alternately in successive rows: spots again.

35. Three equilateral triangles with a small triangular area at the common centre.

41. Ten semicircles near to one another and parallel: the feature of this is the broken shaggy brushes at the ends of the semicircles.

43, 44, 45. A parabola lying within another one of smaller parameter; the lines of light being rather thicker about the vertices. In 44 each vertex has opened, turned the broken edge back and taken a small ball into the open mouth: the bands about the axis, which is not drawn in the original, are diffraction creations: the inner parabola is broken into flakes about the vertex by dark cross lines.

42. An hyperbola and its conjugate, twice repeated, without asymptotes. The flaking appearance is noticeable.

46. Two ellipses, side by side: as a larger circle gives a smaller central spot, the curve at the end of the minor axes gives a smaller spot, and that at the end of the major ones a larger spot: the result is the broadening white line in the figure.

47. Five diminishing circles with internal contact, where the lines are made thinner: here are the shaggy offshoots similar to those in 41.

50. Three circles, near, not quite touching. Arago spots and flaking.

48, 49, 51. Arago spots made by small arcs of circles.

52. A square divided into 4 small squares, in each of these a circle inscribed, not quite touching. Not to mention the small detail, this figure suffers the curious inversion of appearing as 4 circles with inscribed squares.

53. Four circles.

54. A square with an external semicircle on each side.

55. Five small circles in a ring touching one another.

56. Two circles, each through the centre of the other.

57. Two unequal circles, near, not quite touching: the larger spot in the smaller circle, and the flaking disturbance of the larger by the neighbourhood of the smaller.

60, 66. Eight small circles in a ring touching one another: in each case there is the bright spot at the centre of each circle, in 66 there is one at the centre of the whole figure:

the formation of the common tangents at the points of contact is not difficult to imagine.

58, 59. The square and triangle which have turned about and point inwards: their sides have been resolved entirely into transverse flakes.

62. A square with thicker lines of light.

61. Not quite a square, a bright square area with an inscribed dark circular area.

65. A pentagon: here, as in several of the figures just above, there is a bright spot at the centre.

## Fresnel's *Diffraction from Simple Objects.*

67. The inner part shows Fresnel's interference-lines from a bi-prism, with Grimaldi's fringes at the sides.

68, 69. Narrow slits ; 68, with the broader bands, is from the narrower slit. Both slits are so narrow that the exterior bands, through interference of parts of the same wave from one side, do not come in : the bands are given by waves from the two edges. It may be remarked that in exterior bands there is more indication of colour than in interior bands : the neighbouring rays which form exterior bands can travel almost parallel and make coarser bands with more chromatic dispersion. In the case of light passing on to an aperture, care is sometimes necessary to note which of the two effects is predominant.

70, 81. The eye of a bodkin, one to show interior bands, the other to show the exterior bands: it is not easy to develop both effects at once. The bands within the eye are not interference of waves from the two sides, but the exterior bands of each side: it happens that the breadth is such that a band from one side is superposed on one from the other, so the central line is dark.

79. Four round holes of increasing size. This is a case of exterior bands in the bright spaces; the centre of the space may be white or not according to the breadth of the hole: also the rings and spots are brightly coloured. These holes varied from ½ to 2 millim. diameter. If a hole be taken ⅓ millim. diameter, the phenomenon changes and becomes analogous to 68 and 69: concentric spectra are formed in

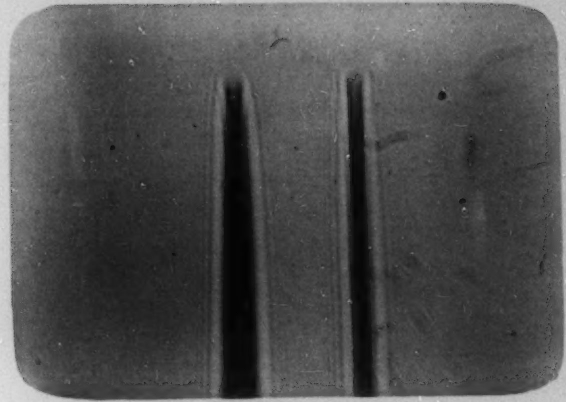

Fig. 71.

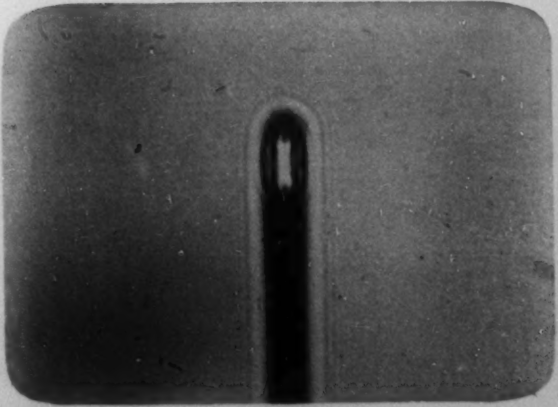

Fig. 72.

the shadow, and there are no rings in the projection of the aperture.

71, 72 (Pl. V.). The points and eyes of ordinary needles: the one with the broadest central line is the shadow of the smallest needle which is made: here the interior and exterior bands both appear.

80. A quartz fibre about ·0005 inch diameter.

73. Wire gauze: each wire gives in shadow 6 dark bands: the spaces give sometimes 2, sometimes 3 bands, showing an inequality of distance. These bands are the exterior bands from the sides of the wire, and give bright colours. The general appearance to the eye is that of a Scotch tartan.

77, 78. Perforated zinc. The former is developed to show the rings in the spaces; these are coloured, and the centre may be white or not according to the size of the holes or their distance from the screen. The latter figure is developed to show the interior bands on the dark parts; they naturally give hexagonal systems. This may illustrate the markings in *Pleurosigma angulatum*, which are regarded as diffraction-bands made by the rows of white spots that form the real structure of the diatom; but, in truth, this case can be realized without the aid of diffraction. Where there are such rows of spots, there must be the lines of shadow between them. The narrowest dark space marked over with diffraction lines has two dark bars separated by a bright central line.

74. Arago's experiment.—The shadow of a threepenny-piece, showing the bright centre. Here parallel sunlight was thrown uncondensed on to the pinhole. The coin was about 18 feet from this, held by a thin wire, and the screen of the camera 18 feet beyond, without any lens. The illumination was not uniform, so that the exterior rings are partly seen: if a lens is used, several rings may be seen around the bright centre, but the complete shadow is too large for the field of view. According to Verdet, Arago employed a circular disk 2 mm. in diameter.

75, 76. Arago's experiment.—Shot fixed on glass; 3 millim., 2 millim., 1 millim. diameter. These were taken with the eyepiece and the ordinary arrangement. In theory there are concentric rings over the whole shadow, but they are more difficult to see than the bright centre. They appear in fig. 76, and in a strong light may be produced with the larger shot. It should be noticed in fig. 75 (Pl. VI.) and fig. 76 how large a bright centre has been made in several places by specks of dust.

Both with the shot and the threepenny-piece, when they are most accurately arranged, as evidenced by the regularity of the rings, a faint dark spot may be seen at the centre of the white spot, and in some positions of the disk relatively to the eyepiece this opens out into a faint dark ring. At present, I have not been able to ascribe with certainty a reason for this secondary effect, but I think it arises because the source of light is not a mathematical point.

83 (Pl. VI.). Conical refraction; external. In conclusion, I venture to pass the strict limits of the subject by showing the crowning triumph of the hypothesis of wave-propagation. Light through 5 minute pinholes passing in a special direction through a crystal of arragonite emerges in 5 cones of light: the four outer circles show by their imperfection the development of the circle from the two points that are formed by a double-refracting crystal.

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Schwerd.—Die Beugungserscheinungen. Mannheim, 1835.

Brewster.—Encycl. Brit. 8th ed. 1858; art. Optics.

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### Discussion.

Dr. **Johnstone Stoney** thought the obtaining of permanent records of diffraction phenomena of great importance, and was particularly interested in the photograph showing conical refraction.

Prof. **S. P. Thompson** said he had never seen diffraction

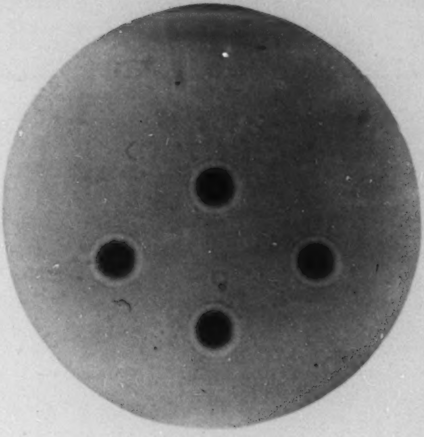

Fig. 75.

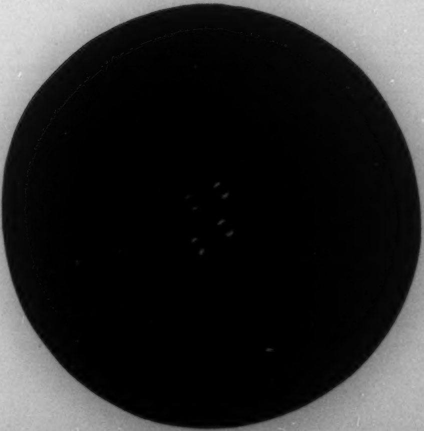

Fig. 83.

effects exhibited to an audience so well before. He noticed that in several of the photographs Arago's spot was unintentionally shown to perfection, in the shadows of dust particles.

The **President** greatly appreciated the fact that the conical refraction photograph had been exhibited for the first time before the Physical Society.

## IV. *The Viscosity of Liquids.*

### *By* Owen Glynne Jones, *B.Sc.*[*]

The object of this paper is to point out a method for the accurate determination of the viscosity of highly viscous liquids. The author would prefer to delay the publication of most of his results till the experiments are completed. The advantages and disadvantages of the method, and its applicability to the determination of viscosities such as those of alcohol and water, are not yet entirely ascertained, but such of these points as have already suggested themselves will be noticed at the end of the paper.

Sir G. Stokes has long since shown that if a sphere moves vertically in an infinite liquid under the action of gravity only, it in course of time assumes a constant speed :

$$V=\frac{2}{9}ga^2\frac{(\sigma-\rho)}{\mu},$$

where $a$ is the radius of the sphere, $\sigma$ its density, $\rho$ that of the liquid in which it moves, and $\mu$ the viscosity of the liquid. The equation assumes that there is no slipping at the surface of the sphere, *i. e.*, that the coefficient of sliding-friction is infinite. The effect of such sliding-friction would be to modify the equation thus :

$$V=\frac{2}{9}ga^2\frac{\sigma-\rho}{\mu}\frac{\beta a+3\mu}{\beta a+2\mu},$$

where $\beta$ is the coefficient of sliding-friction.

The method employed by the author consists in the measurement of the downward speed of a sphere of mercury through the viscous liquid. The amount of mercury used is taken sufficiently small to render possible the measurement, correct to ·1 per cent., of the time taken to pass through a distance of about 25 centim. This also renders legitimate the assumptions that the mercury remains spherical during its motion, and that the liquid in an ordinary burette about 1·5 centim. internal diameter is for purposes of calculation of infinite extent, the motion of such a sphere falling down the burette along its centre line being unaffected by the sides of the vessel.

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[*] Read February 9, 1894.

The burette is jacketed with water kept as nearly as possible at constant temperature. The temperature of water direct from the main was observed last autumn to vary to an extent of only ·03° C. in an hour and a half, and good results were then obtained for the viscosity of glycerine. Within the last fortnight the main temperature has not been nearly so constant, and more has been learnt concerning the variation of viscosity with temperature than the absolute value of viscosity for any definite liquid.

The mass of a sphere of mercury suitable for glycerine would be between ·003 and ·010 grm. This is too small to be determined with sufficient accuracy by direct weighing, with a balance estimating to one tenth of a milligramme. But there is no necessity to determine such a mass directly.

Let a mass of mercury weighing about ·1 grm. be taken and weighed carefully. Let it be divided into about 12 parts, approximately equal to each other. Let the speed of each through a column of very viscous liquid, such as glycerine or clear castor-oil, be determined. Then, using Stokes's result,

$$\mu \propto \frac{a^2}{v},$$

$$\therefore \quad \mu \propto \frac{m^{\frac{2}{3}}}{v};$$

and for a given liquid with constant viscosity

$$m \propto v^{\frac{3}{2}},$$

or

$$m = kv^{\frac{3}{2}}.$$

Hence

$$\Sigma m = k\Sigma v^{\frac{3}{2}}.$$

But $\Sigma m = \mathrm{M}$, the whole mass of mercury, and $\Sigma v^{\frac{3}{2}} = \mathrm{V}^{\frac{3}{2}}$, the speed that the whole mass would have if it fell as a sphere through the infinite liquid. Perhaps taken as a whole the mercury would not fall as a sphere, and the liquid in the burette would not be as of infinite extent; but by this subdivision such errors are avoided.

We thus get the speed V corresponding to the mass M, and these values can be applied at once in the equation

$$\mu = \frac{2}{9} g a^2 \frac{(\sigma - \rho)}{\mathrm{V}},$$

or

$$= \frac{2}{9} g \left( \frac{3\mathrm{M}}{4\pi\sigma} \right)^{\frac{2}{3}} \frac{\sigma - \rho}{\mathrm{V}};$$

for

$$\mathrm{M} = \frac{4}{3} \pi a^3 \sigma, \quad \text{and} \quad a^2 = \pi \left( \frac{3\mathrm{M}}{4\pi\sigma} \right)^{\frac{2}{3}}.$$

Moreover the mass of each of the smaller spheres may be easily estimated, since

$$\frac{m}{\mathrm{M}} = \left( \frac{v}{\mathrm{V}} \right)^{\frac{3}{2}},$$

and

$$m = \left( \frac{v}{\mathrm{V}} \right)^{\frac{3}{2}} \mathrm{M}.$$

The author has been able in this way to determine the mass of a small sphere (and hence its radius) weighing about ·003 grm., correct to four significant figures. Having thus determined its dimensions, it may be employed for other liquids than that by which these dimensions were obtained.

But the important question suggests itself whether $\mu$ is simply inversely proportional to the speed of the falling sphere, or whether, as some maintain, there is a finite coefficient of sliding-friction, and a definite amount of slipping at the surface, which will render the connexion between $v$ and $m$ much more complicated.

This may be tested in a simple manner by observing the speed V for a small mass, dividing it into two parts, and observing the speeds $v_1$ and $v_2$ for each part in the same viscous liquid at the same temperature. If there be no sliding-friction,

$$\mathrm{V}^{\frac{3}{2}} = v_1^{\frac{3}{2}} + v_2^{\frac{3}{2}}.$$

If sliding-friction exists the effect will be to render the V calculated in the above equation from $v_1$ and $v_2$ greater than the observed speed for the undivided mass, the divergence being most clearly shown when the two parts are as nearly as possible equal to each other.

For let us assume that the whole is divided into two equal parts, and that the two speeds observed are V and $v_1$, corresponding to the two radii A and $a$.

Now $A^3=2a^3$, and A is therefore $=2^{\frac{1}{3}}a$.

With sliding-friction,

$$V=kA^2 \cdot \frac{\beta A+3\mu}{\beta A+2\mu},$$

$$=2^{\frac{2}{3}}ka^2 \cdot \frac{1{\cdot}26\beta a+3\mu}{1{\cdot}26\beta a+2\mu},$$

and

$$v=ka^2 \cdot \frac{\beta a+3\mu}{\beta a+2\mu},$$

then the speed calculated for the whole mass from the formula

$$V^{\frac{3}{2}}=v_1^{\frac{3}{2}}+v_2^{\frac{3}{2}}=2v^{\frac{3}{2}}$$

would be

$$V'=2^{\frac{2}{3}} \cdot ka^2 \cdot \frac{\beta a+3\mu}{\beta a+2\mu}.$$

The ratio of $\frac{V'}{V}$ is therefore

$$\frac{\beta a+3\mu}{\beta a+2\mu} \cdot \frac{1{\cdot}26\beta a+2\mu}{1{\cdot}26\beta a+3\mu}.$$

Since all the quantities involved are positive, this ratio is evidently greater than unity. As $\beta$ varies from $\infty$ to zero, the value of the ratio increases from 1 to a maximum $1+k$, and then diminishes to 1 again. Thus the divergence between the calculated and the observed speeds does not become greater as the coefficient of sliding-friction diminishes, although this divergence is actually due to the sliding.

Taking the value ·04 centim. for the radius of the sphere, the maximum value of $k$ will be $\frac{1}{44}$, the divergence thus amounting to about 2½ per cent. The ratio $\frac{\mu}{\beta}$ that gives this result is $\frac{1}{55}$ or $\beta=55\mu$.

If we assume $\frac{\mu\rho}{\beta}$ to have the same value for glycerine that Helmholtz assigns to water, the difference between the observed and the calculated speeds will amount to about 1 in 144 for such spheres ($a=\cdot04$ centim.) as were employed in the investigation.

Various experiments were recently made by the author to test these results; considerable difficulty was experienced in keeping the temperature constant, except when this was 0° C. The tests hitherto made are not regarded as final, and the author would prefer to defer their publication until the series of experiments is complete. But the divergences from the simple law as at first assumed are in all cases within the limits of experimental error, and the method of determining viscosity is not shown to be defective by those test experiments. The temperature difficulty is not so serious in the case of colza-oil, which is one of the liquids experimented upon. The error involved with speeds not exceeding 2 centim. per second through that liquid did not range beyond $\pm0\cdot2$ per cent., and it was as usual to get positive errors as to get negative. Times were estimated only to the same degree of accuracy.

It is possible that sliding may occur if the speed of the sphere M exceeds a certain limiting value. This also is obviated by determining its speed indirectly as $(\Sigma v^{\frac{3}{2}})^{\frac{2}{3}}$, since each individual portion travels so much more slowly.

There is another reason why better results may be expected by this process of subdivision. Mercury is liquid, and a sphere would be deformed if it passed rapidly through the viscous medium. Its speed would be diminished, and it could not be dealt with directly by the fundamental equation connecting $\mu$ and V. But by subdivision the masses and speeds dealt with are reduced to such an extent that we may confidently assume the shapes to remain spherical. If the deformation thus produced were appreciable, it could again be manifested by the application of the formula

$$V^{\frac{3}{2}}=\Sigma(v^{\frac{3}{2}}).$$

The calculated V′ would be greater than the observed V, the error being of the same sign as that produced by the neglect of any possibly existing sliding-friction.

The error produced by the sides of the burette, which may be so near as to retard the downward motion, is also diminished by the subdivision of the original mass. This also would have the same sign as the other errors specified. The simplest way of testing its existence is to insert into the upper portion of the burette-tube a thin glass cylinder of smaller diameter, and to send down a sphere along the axis of these two concentric cylinders. In the upper portion of its path the sphere is at a smaller distance from the boundary of the liquid than in the lower portion. If the sides actually affect the motion, the speed of the sphere will suddenly change when it enters into the wider portion of the liquid column. If the change of speed is not appreciable, it may be assumed that the diameter of the burette is sufficiently large.

It has hitherto been assumed that we have the means of keeping the temperature of the liquid constant. This is of the utmost importance, inasmuch as the temperature-variation of viscosity is rarely inconsiderable. The viscosity of glycerine changes from 45 to 8 in the range of 16° from 4° to 20° C. At a temperature of 15° C. there is a 10-per-cent. variation per degree change. This implies that to get the viscosity correct to four significant figures the thermometers employed should read to ·01° C.

In the case of olive-oil, using Osborne Reynolds's empirical formula for the viscosity at any temperature between 15° and 50° C.,

$$\mu = 3{\cdot}265\, e^{-{\cdot}0123\, t}.$$

Any such equation, $\mu = Ae^{-kt}$, means that the percentage variation per degree is constant, since its differential equation is

$$\frac{d\mu}{\mu\, dt} = \text{constant}.$$

For olive-oil this constant is ·0123 and the percentage variation is 1·23 for any temperature within the given limits—about one ninth of the change in the viscosity of glycerine per degree. In this case the thermometer should read to $\frac{1}{12}$

of a degree. It is useless to calculate the viscosity of glycerine beyond the fourth significant figure unless there be means for the accurate determination of temperature correct to at any rate ·001° C.

The liquids experimented upon are all bad conductors of heat, and though this is advantageous in that the change of temperature during the course of an observation is not likely to be great, it is a disadvantage in that it takes a long time for the temperature to become uniform throughout the length of the column of liquid. It is quite possible for a difference of temperature of ·1° C. to exist at points in the liquid 1 dcm. apart even though the water has been circulating in the jacket for some minutes.

The temperature can only be expected to be uniform when the circulation has been of constant temperature for about 20 minutes.

But it is of importance to note that small variations in the temperature of the liquid at different points along the path of the falling sphere need not trouble us much if the mean temperature be known. And, similarly, small changes in the mean temperature of the whole during the course of an experiment may be harmless if the mean temperature during the interval be known.

For it can be proved that the speed of flow of a body is the speed corresponding to the mean temperature, however the temperature may vary along the length, if the speed be small and if the temperature-variation be small. Both these conditions are satisfied in the actual experiments undertaken. The inertia of the body is so small that it almost instantly assumes the limiting speed corresponding to the temperature of that part of the liquid through which it is moving.

Let the temperature vary from $\theta_1$ at one end to $\theta_2$ at the other end of the column of length $l$. Let the corresponding viscosities be $\mu_1$ and $\mu_2$; and let $\theta$ and $\mu$ be the temperature and viscosity at a point at distance $x$ from the top of the column.

For the small change of temperature assumed,

$$\frac{\mu-\mu_1}{\mu_1-\mu_2}=\frac{\theta-\theta_1}{\theta_1-\theta_2},$$

or

$$\mu = A(\theta_1 - \theta) + \mu_1.$$

Now, if $dt$ be the time taken to traverse the distance $dx$, the general equation of steady motion gives us

$$dt = \frac{\mu\, dx}{k}$$

$$= \frac{1}{k}\{\mu_1 + A(\theta_1 - \theta)\}dx.$$

Let $\theta = f\textcircled{x}$, such that

$$\theta_1 = f\textcircled{0} \quad \text{and} \quad \theta_2 = f(l).$$

Then the time taken for the whole descent

$$T = \frac{1}{k}\int_0^l \{\mu_1 + A(\theta_1 - \theta)\}\, dx$$

$$= \frac{1}{k}\left\{\mu_1 l + A\theta_1 l - A\int_0^l f\textcircled{x} dx\right\}.$$

But

$$\int_0 f\textcircled{x} dx = B, \text{ the area of the temperature-curve,}$$

$$= l\,.\,\theta_m, \text{ if } \theta_m \text{ be the mean temperature ;}$$

$$\therefore \quad T = \frac{1}{k}\{\mu_1 + A(\theta_1 - \theta_m)\}l.$$

But if the temperature had been uniformly $\theta_m$ throughout the length $l$, the time $\tau$ would have been

$$\tau = \frac{l}{k}\,\mu_m,$$

where

$$\mu_m = \mu_1 + A(\theta_1 - \theta_m).$$

Hence $$T = \tau.$$

It therefore is only necessary to determine the mean temperature during the interval, and even this is unnecessary if our object is to compare two masses of mercury by their speeds, if they are made to follow each other sufficiently rapidly for the mean temperatures to remain constant in the two cases.

If a variation in temperature along the tube be suspected, the test is simply to send down a minute sphere and observe its speed for short lengths all along the tube. This speed is constant if the temperature is uniform. In accurate estimations of absolute viscosity the variation in speed should not exceed 1 in 1000 along the tube.

It is probably preferable to read the temperature by a thermometer inserted in the viscous liquid, using a burette of sufficient bore to render the insertion safe. But good results have been obtained with the thermometer in the water-jacket, tied close to the inner tube ; this arrangement serves quite well when the water-jacket is fairly constant in temperature.

An observation with glycerine cannot be called good if the temperature-variation exceeds ·03° C., and any that are made with greater variation must be discounted. This conclusion is forced upon one when the periods of falling are taken for the same sphere twenty or thirty times in succession. The curve plotted, connecting the temperature with the time of falling, is a straight line within a range of 1° C., and it is generally found that the points farthest from the straight line correspond to the greatest variation of temperature during the fall. Such a curve supplies us with the means of determining the correction necessary to reduce a speed at one temperature to that at another.

To ensure that the falling sphere shall remain in the axis of the burette, the burette and its jacket are mounted vertically on a stand fitted with levelling-screws, such as that of an ordinary Jolly's balance. The mercury is let down into the burette by a small funnel. The speed is determined by observing the time taken to pass from one mark to another. The distance taken was generally about 50 centim., measured correct to ½ millim., the time taken to traverse that distance being from 100 to 200 seconds. The time was measured with an ordinary watch beating fifths-seconds, or more recently with a Siemens chronograph. In either case the masses of mercury were so chosen that the probable error in a single observation was 1 in 1000.

The following results are for glycerine at temperatures of 18°·28 and 4°·35 C. The former agrees closely with a value obtained by interpolation from Schöttner's results. The latter would appear to be considerably higher than the corresponding interpolation.

A. Mass of mercury taken, ·03737 grm. This was divided into 12 parts—*a*, *b*, *c*, *d*, &c. . . . *l*.

Greatest variation in temperature during a single observation = ·01° C.

Greatest variation in temperature during whole interval = ·03° C.

Length of path employed, 50·28 centim.

Ordinary watch used to determine time.

Mean temperature, 18°·28 C.

| Mass. | Mean temp. | Time. | Time corrected to 18°·28 C. | $v^{\frac{5}{3}}$. | Mass, *m*. |
|---|---|---|---|---|---|
| | ° | seconds. | seconds. | | grm. |
| *a* ...... | 18·27 | 128·2 | 128·0 | ·2462 | ·003516 |
| *b* ...... | 18·27 | 121·4 | 121·2 | ·2672 | ·003815 |
| *c* ...... | 18·27 | 135·2 | 135·0 | ·2273 | ·003245 |
| *d* ...... | 18·27 | 132·4 | 132·2 | ·2346 | ·003349 |
| *e* ...... | 18·27 | 117·2 | 117·0 | ·2817 | ·004022 |
| *f* ...... | 18·28 | 137·8 | 137·8 | ·2204 | ·003146 |
| *g* ...... | 18·29 | 197·2 | 197·4 | ·1285 | ·001835 |
| *h* ...... | 18·29 | 148·6 | 148·8 | ·1963 | ·002804 |
| *i* ...... | 18·29 | 160·8 | 161·0 | ·1746 | ·002492 |
| *j* ...... | 18·29 | 131·2 | 131·4 | ·2367 | ·003380 |
| *k* ...... | 18·29 | 136·0 | 136·2 | ·2244 | ·003204 |
| *l* ...... | 18·29 | 157·8 | 158·0 | ·1795 | ·002564 |
| | | | | Σ = 2·6174 | Σ = ·037372 |

Taking

$$\sigma = 13{\cdot}59 \quad \text{and} \quad \rho = 1{\cdot}26,$$

$$g = 981,$$

$$\mu = 83{\cdot}9 \times 12{\cdot}33 \left(\frac{\mathrm{M}}{13{\cdot}59 \times 2{\cdot}617}\right)^{\frac{2}{3}},$$

$$= 10{\cdot}69 \text{ for the mean temperature } 18^{\circ}{\cdot}28 \text{ C.}$$

B. Mass of mercury taken, ·1096 grm. This was divided into 10 parts.

Greatest variation in temperature during a single observation = ·07° C.

Greatest variation in temperature during whole experiment =·22° C.

(This result is therefore not so reliable as the previous one.)

Mean temperature, 4°·35 C.

Siemens chronograph employed to measure time.

Length of path employed, 50·28 centim.

| Mass. | Mean temp. | Time. | Time corrected to 4°·35 C. | $v^{\frac{3}{2}}$. | Mass, *m*. |
|---|---|---|---|---|---|
| | ° | seconds. | seconds. | | grm. |
| *a* …… | 4·30 | 111·6 | 111·1 | ·08401 | ·01080 |
| *b* …… | 4·32 | 101·4 | 101·1 | ·09680 | ·01244 |
| *c* …… | 4·45 | 116·1 | 117·2 | ·07751 | ·00996 |
| *d* …… | 4·28 | 123·1 | 122·4 | ·07265 | ·00934 |
| *e* …… | 4·41 | 99·8 | 100·4 | ·09782 | ·01257 |
| *f* …… | 4·48 | 150·5 | 152·3 | ·05236 | ·00673 |
| *g* …… | 4·23 | 89·75 | 88·77 | ·11760 | ·01512 |
| *h* …… | 4·32 | 107·4 | 107·1 | ·08876 | ·01141 |
| *i* …… | 4·40 | 108·3 | 108·8 | ·08667 | ·01114 |
| *j* …… | 4·50 | 114·3 | 115·9 | ·07885 | ·01014 |
| | | | | $\Sigma =$ ·85303 | $\Sigma =$ ·10965 |

Thus $\mu_{4^\circ\cdot 35\text{ C.}} = 46\cdot 27$.

The value of $\Sigma v^{\frac{3}{2}}$, when no corrections are made for temperature, is found to be

$$V^{\frac{3}{2}} = \cdot 85434,$$

which agrees fairly well with the above result.

The temperature-variation of viscosity is considerable. It is of practical importance in certain applications, as, for example, in the use of viscous liquids for lubricating purposes. A special piece of apparatus was used by the author to investigate this variation for different liquids.

It consists of a glass tube closed at each end, with a lateral tube fixed at right angles to its middle portion and forming an outlet. The vessel is filled with the liquid and a very minute sphere of mercury is inserted. A thermometer passes through a stopper that encloses the liquid, the bulb of the thermometer reaching just up to the main tube. The vessel is immersed in a copper water-bath so that the main tube is vertical and the thermometer horizontal. The thermometer passes out of the bath through a small stuffing-box on one side. A window of glass is inserted in the opposite side of the bath through which the motion of the mercury may be observed. As soon as the mercury has fallen to one end of the tube, it is reversed and the mercury allowed to fall down to the other end again.

The thermometer reads the temperature of the viscous liquid at its middle, this being very nearly the mean temperature. The bath is heated slowly to about 50° and then allowed to cool, during both of which operations the times of descent of the mercury from one fixed mark to another are carefully noted through the window, the water being stirred constantly. The times of descent are proportional to the viscosities, if a slight correction be made in each case for the variation in the densities of the mercury and the liquid, with change of temperature.

To illustrate the nature of this correction let us take the case of glycerine,

$$\mu = k\,\frac{(\sigma-\rho)}{\sigma^{\frac{2}{3}}}\,\mathrm{T},$$

where T is the time of falling, and $\sigma$ and $\rho$ are the densities of mercury and glycerine respectively.

If $s$ and $r$ are the corresponding coefficients of expansion,

$$\mu = k\,\frac{(\sigma_0-\rho_0)-t(\sigma_0 s-\rho_0 r)}{\sigma_0^{\frac{2}{3}}}\,(1+\tfrac{2}{3}\,st).$$

This is approximated by taking $s=\dfrac{1}{5500}$ and $r=\dfrac{1}{1000}$,

$$\mu = \mathrm{K}(12{\cdot}34+{\cdot}0002\,t)\mathrm{T}.$$

The correction is therefore unnecessary between 0° and 30°, and is only 1 in 1200 from 30° to 70°. For ordinary temperatures it may therefore be neglected.

With a relative viscosity-curve thus obtained, and with one good absolute determination, we have the means of calculating the absolute viscosity at any temperature along the range.

Conversely, we have the means of estimating small masses of mercury by their speed of flow through glycerine or any other known liquid at a known temperature, or of estimating the mean temperature of the liquid.

For example, if a column of liquid be heated from above till its state of temperature becomes constant without the aid of convection, we can here determine the temperature-curve along its length, and in fact employ Forbes's method to determine the thermal conductivity of the liquid at various temperatures.

In concluding this description of the methods now being employed for the determination of absolute and relative viscosities, it may be well to remark on the advantages and disadvantages of these methods that have already manifested themselves. In the first place we are dealing with steady motions, and are able to investigate the phenomena attending a constant rate of shearing in the liquid much more satisfactorily than if we observe an oscillating motion such as that of Coulomb's disk or Helmholtz's sphere. The existence of sliding-friction can be directly tested, not only between mercury and the more highly viscous liquids, but also between any two liquids that do not dissolve each other. Thus spheres of water may be used with nearly all the fixed oils, and spheres of oil of cloves (density 1·0475) or of oil of myrrh (density 1·0189) may be used with water.

The apparatus is simple and inexpensive ; results may be rapidly obtained when a few standard mercury spheres are preserved. They should be kept in a sample of the viscous liquid to be tested. If a sphere breaks, the pieces should be washed in water and reunited on hard pressed blotting-paper. The quality of oils is often tested by their viscosity, and special viscosimeters on the capillary-tube principle of Poiseuille are used for the purpose. A time-reading through a sample of the oil with a standard mercury sphere offers an expeditious way of testing. If the oil is thin and the mercury falls too fast, a calibrated water sphere may be used instead. A sphere of water of 1 millim. radius, coloured with eosin to be clearly visible, travels at the rate of one inch per hour in castor-oil at 8° C. ; and here in parenthesis it may be added that we have by far the simplest method of observing the time-integral of temperature for small ranges.

The general method cannot be employed for opaque liquids, as we wish to observe the falling sphere; but it is probable that with a little ingenuity this difficulty could be overcome if the opaque liquid presented itself for examination. The small inertia of the falling sphere, advantageous as it is in exhibiting the slightest variations of temperature, is a serious objection if small solid particles are held in suspension in the liquid. As a rule these particles will avoid the small sphere and not touch it; but in the event of contact occurring there is the likelihood of a permanent union between the two and of the particle being dragged down with the sphere, with consequent loss of speed of the latter. Hence clear liquids must be used.

The author wishes to acknowledge his obligations to Prof. Henrici for very kindly rendering available the apparatus of his laboratory for the needs of the above experiments.

## DISCUSSION.

Prof. EVERETT, in a written communication, suggested that the motion of the liquid sphere be checked by using beads of quartz or glass.

Lord RAYLEIGH pointed out in a letter that the formula employed related to a solid sphere, and thought it not legitimate to use it for liquid spheres, for the tangential forces at the surface would set the interior liquid in relative motion, and modify the resistance experienced. He also thought the existence of a finite coefficient of sliding friction between two fluids an impossibility.

Mr. WATSON said temperatures might be kept constant for days together by Ramsay and Young's vapour-jacket.

Dr. SUMPNER thought the surface-tension of such small spheres of mercury was so very large that they would act practically like solids. The want of solidity might be of importance when the two liquids were very nearly alike in density and other properties.

Mr. BLAKESLEY said that at high velocities the falling sphere might acquire a palpitating motion in addition to the gradual descent, and this might introduce errors.

Prof. PERRY considered that the experiments on the velocity of a small sphere, and those of the two parts in which it was divided, which showed that

$$V^{\frac{3}{2}} = v_1^{\frac{3}{2}} + v_2^{\frac{3}{2}},$$

proved the simple formula used to be correct.

Mr. Boys inquired if any tests had been made on the constancy of dimensions of the spheres used. He would expect that in the case of water and oil, for example, that mutual contamination would take place. Speaking of the indirect method of determining the masses of small spheres, he thought direct weighings might be made, for, as the President and Prof. Poynting had shown, the balance might be immensely improved.

Prof. S. P. Thompson suggested that small globules of aluminium or slag might be used.

Dr. C. V. Burton thought Lord Rayleigh's criticism important, and that large corrections might be necessary. He failed to see how the large surface-tension mentioned by Dr. Sumpner could prevent internal circulation.

Mr. Trotter said Lord Rayleigh's point might be tested by using a sphere of oiled wax.

Mr. Boys mentioned that Lord Rayleigh had shown in the case of soap rings that variation of surface-tension, due to stretching or compression, produced stability. The same phenomena would probably retard internal circulation.

The President said there was little doubt that internal circulation as mentioned by Lord Rayleigh would modify the velocity.

In his reply Mr. Jones said he could not imagine how, in pure liquids, internal motion in the falling spheres could be set up. In answer to Mr. Boys, he had found slight changes in the masses of the water spheres after being used many times, but this was a question of days. During an ordinary series of observations the dissipation was too small to be observed.

After the meeting had been adjourned Mr. Boys and Dr. Burton considered the question of internal circulation, and the latter pointed out that with perfectly liquid spheres there would be infinite slip, and the coefficient of sliding friction $\beta$ would be zero. The velocity of descent would therefore be $\frac{3}{2}$ times that given by the first equation.

## V. *On the "Magnetarium."* *By* H. WILDE, *F.R.S.*

(Abstract.)

Mr. WILDE exhibited and described his "Magnetarium" (March 9, 1894).

This consists of a hollow geographical globe wound all over the inner surface with insulated wire in planes parallel to the equator. Within this globe is a sphere wound with wire on its surface, and having its axis inclined at 23½° to that of the outer pole. By means of epicyclic gearing the spheres can be made to rotate at slightly different rates. When electric currents of suitable strength are passed through the two windings, the magnetic condition of the earth can be imitated, both as regards distribution at any epoch and the secular variations. A better result was obtained by putting sheet iron over the land areas, and a still closer approximation by using thin iron over the water areas. A magnetic chart and tables giving the magnetic elements at various places for different epochs were shown. The author mentioned that recent observations by the United States Survey at Ascension Island, and by Prof. Thorpe in Senegambia, had confirmed results obtained by the magnetarium.

### DISCUSSION.

The PRESIDENT said he had tried the apparatus, and found the Siberian oval closely imitated. The secular variations at Greenwich were also well shown. In South America the approximation was not so good.

In reply to a question by Mr. Blakesley, Mr. WILDE said the present position of the pole of the inner sphere was 84° W., 67° N.

## VI. *A new Electrical Theorem.*

*By* THOMAS H. BLAKESLEY, *M.A.*[*]

THE very short paper which I shall read to the Society contains the account of a Theorem which, though admitting of easy proof, appears, so far as my inquiries have gone, to have hitherto escaped notice.

In order to state the matter briefly, it will be well to adopt the following definition :—

If in any system of conductors, however reticulated, two or more modes of disposition of sources of electromotive force produce in every part of the network the same current, such systems of disposition are called *equivalent systems.* Then the theorem is as follows :—In any system of conductors, possessing seats of electromotive force at any number of points, if any of these sources be supposed to move continuously along the various bars of the conducting system, and, where a point of junction is encountered, each to become a seat of the *same* electromotive force in *each* of the newly encountered bars (of course leaving the resistance of the source behind), then the disposition at any moment is equivalent to that at any other moment, and therefore to the original disposition. [Of course the direction of the electromotive force must be carefully maintained the same: if it is towards the knot before crossing it, it must be away from the knot after passing it.] The proof need only refer to the passing of a knot point, for no one will doubt that if the sources only move in an *unbranching* portion of the conductor the currents in different parts of the system will remain the same.

Let therefore the source $e$ approach the point A at which its path splits into $n$ other ways. In each of the $n$ bars suppose a source $e$ inserted as directed, then these $n$ alone must be equivalent to the single source before reaching A; for if the $n$ sources are reversed, the current due to these sources in every portion of the system is reduced to zero. The reversed $n$ sources would therefore alone produce currents in the system equal numerically, but opposite in direction, to those produced by the single source. Hence it follows that the $n$ sources (not reversed) will produce the same current as the single source.

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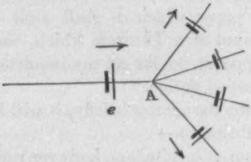
[*] Read February 23, 1894.



The principle of the superposition of currents enables us to apply this result to each source of the system, and therefore to prove the truth of the theorem in its complete generality.

In equivalent systems, since the current in every part remains the same, the total power expended remains the same; and equivalent systems might have been defined as those which produce the same expenditure of power in each part; and therefore the total power of the sources remains the same.

From the point of view of Kirchhoff's theorem $\Sigma e = \Sigma . rc$ for any closed path in a network, the above general theorem may seem to some minds even plainer and more easily proved than on the method of demonstration which I have employed. For it is plain from the method of derivation, that if a seat of electromotive force exists in any closed Kirchhoff path it can never leave it; and if in the movement of the sources one of them approaches the closed path under consideration, at the encounter it becomes in that path two equal sources acting in opposite directions.

If, therefore, $\Sigma e$ remains the same for any path and $r$ remains the same for every part, then obviously $c$ must remain the same for any portion of that path, and therefore for every part of the network.

The following propositions flow immediately from the main proposition :—

(1) If a closed continuous surface contains any region of any network, and some bar which cuts the surface contains, or by derivation as above can be made to contain, the seat of an

electromotive force, then that source can be done away with without disturbing the currents in any portion of the system provided that in the other bars which cut the surface sources of electromotive force be inserted of equal value but of opposite direction as regards inside and outside of the surface; for it is clear that such sources would result from the migration of sources in one direction.

(2) If two systems of electromotive forces are equivalent, one may be derived from the other. For if system A is equivalent to system B, and we suppose $\frac{A}{2}$ to represent a distribution identical with A as regards positions, but of half the electromotive force in any case, then $\frac{A}{2}+\frac{B}{2}$ is equivalent to A or B alone. Now if any Kirchhoff path containing a source from $\frac{A}{2}$ does not also contain a source from $\frac{B}{2}$, then Kirchhoff's law would be outraged; for the sum of the electromotive forces in that path would be only half what they are from A alone, whereas the currents and resistances remain the same. Hence for every Kirchhoff path there must be equal sources from each system. Either system may now have its elements moved up to those of the other system; any resulting side branchings will be the same (though differing in sign) whether derived from $\frac{A}{2}$ or from $\frac{B}{2}$, and must necessarily produce no effect by themselves, because if we consider $\frac{B}{2}$ to be reversed, the whole effect of $\frac{A}{2}$ and $\frac{B}{2}$, *now in the same bars*, will be zero.

## VII. *The Attachment of Quartz Fibres.*

### *By* C. V. Boys, *A.R.S.M., F.R.S.*[*]

Members of the Physical Society may remember that in 1887[†] I described a method of making fine fibres of glass and other materials, but especially of melted quartz, which latter had properties of great value, rendering them more suitable for experimental work of combined delicacy and accuracy than those of other known materials. Experiments made since by others as well as myself have further shown that for delicate work of the highest degree of accuracy they are essential.

The method of fastening them, however, at their ends to the pointed end of the torsion-pin at the top or of the suspension below by shellac varnish, or better by melted shellac, is apt to give rise, more especially if the fibre is unskilfully laid in place so that it is twisted round the point, to a slow creeping of the point of rest due to slow changes in the shellac. This, except for the first few days, can hardly ever be of an amount to seriously affect any observations; in fact I have made many observations of the effect of gravitation between small masses with fibres so fastened of a great degree of accuracy, besides those with the radiomicrometer, pocket electrometer, &c., without any inconvenience, yet I have felt that some method of attaching them which would be less likely to hold the fibre by a part in a state of torsional strain or of flexure would be preferable. If the part of the fibre held could certainly be in its natural position and state with respect to the rest, then, even if the fastening should fail to be as perfect as a true weld, any resulting change of zero should be small compared to that observed where the portion held is twisted or much bent.

The process of silvering, electro-coppering, and soldering is an obvious one, but it is not so easily carried out with a fair degree of certainty and in a manner which is convenient of application, as might be expected. My experience of last autumn has enabled me to perform the process in a series of operations, each simple enough, and, as far as I am able to test it in the apparatus with which I am now measuring the Newtonian constant of gravitation (which I may say is of unusual delicacy), with perfect success. In this case the fibre is necessarily stretched to not far from its breaking weight, and it is in such cases that the stability of the fastening is most severely tried.

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[*] Read February 23, 1894.

[†] Proc. Phys. Soc. vol. ix. p. 8.

The first thing I found was that it was a mistake to solder the fibre to the torsion-rod and to the suspension directly. The difficulty of the manipulation is great and a change of fibre is very troublesome. The preferable plan is to solder the ends of the fibre to little tags of metal so small and light that they may be picked up by the fibre from anything on which they rest without risk of snapping the fibre at the point of junction. These tags, which are conveniently made of copper-foil, five millimetres long and one millimetre wide about at the wide end, tapering nearly to a point, can afterwards be fastened to the torsion support and the suspension by shellac varnish or by melted shellac, and now the enormous surface and the stiffness of the foil is sufficient to prevent any trouble from the causes to which reference has already been made.

These tags might also for some purposes, either or both of them, be made of T-form to hang in a pair of V's, and so dispense with cement altogether, and allow of the easy interchange of suspensions or of fibres, but I have not myself employed such a form.

The following operations are those which I have found to answer :—

1. Select a fibre of the right diameter to give the desired torsion. Since the torsion depends on the fourth power of the diameter, a small change in the diameter makes a fourfold change in the torsion, and great accuracy of measurement is needed where an exact torsional rigidity is required. Cut off a piece from two to three centimetres longer than will ultimately be required.

2. Fasten to the extreme ends of the fibre, with melted shellac, little weights of gold or platinum heavy enough to pierce a liquid surface.

3. Hang the fibre over a fixed round horizontal rod of wood, 1 centimetre in diameter or thereabouts, so that the little weights hang side by side, and lift up from below a little glass of strong nitric acid, so as to wet and clean the fibre well above the final points of attachment. The vessel must be wide enough to prevent capillarity from drawing the fibres to one side, or it must be brimful so that the surface is convex, which with nitric acid is objectionable. The vessel must be moved both upwards and downwards past the place at which the weights pass through the surface very rapidly, practically with a jerk; otherwise the weights will be drawn together by capillarity, and the fibres will get twisted, or capillarity will give trouble somehow. With the rapid movement the little weights hardly acquire any pendular motion.

4. After a minute or two do the same, but to a slightly greater depth, with water which may be distilled.

5. When the acid may be supposed to be washed off, immerse in the same way in Rochelle salt silvering-solution (Kohlrausch, 'Physical Measurements,' p. 115).

6. Wash as in 4.

7. Fill a glass with the copper solution that is employed in electrolytic measurements of current, *i.e.* not saturated, and slightly acid. Dip the extreme point of the positive wire from a single cell into the liquid, and with a clean smooth negative wire take the hanging ends, one at a time, and having made the contact outside the glass by resting the upper part of the silver coat upon the wire, let down into the solution, keeping the fibre in gentle movement on the wire and making it dip more and less in the liquid. In a few seconds the little weight will be bright red, and the immersed portion of the silvered coat will be bright red also. The silver coat has sufficient resistance to prevent unduly rapid deposition. Do the same to the other end.

8. Cut off to length, allowing about 5 millimetres at each end for the junction. Take tags of copper-foil three or four centimetres long and three or four millimetres wide, tapering to a point, and having tinned the pointed end of each with the minimum of solder, again wet with chloride-of-zinc solution. On the wet surface lay the coppered end, taking

care that it points in the right direction. Capillarity will now hold it. Rapidly heat the copper to the melting-point by holding a point about one centimetre from the narrow end over a minute flame. The solder will flash and envelope the coppered fibre. Cut off the tag of the desired length, holding the metal by the tag with a pair of pliers and not by the heavy end.

9. Wash in boiling water as in 4 to remove chloride of zinc. The fibre is now attached, but the protruding silver and copper give a want of definiteness in the place of attachment.

10. Dip up to the point of the tag in melted beeswax, following the precautions given in 3, but the two tags may be more conveniently dipped separately.

11. Dip up to the top of the copper and silver in strong nitric acid.

12. Wash in boiling water, which removes acid and beeswax and leaves the fibre ready for use.

13. If it is required to conduct electricity, as for instance to keep the needle of a quadrant electrometer electrically connected with a battery, the whole may now be silvered in a long tube and washed, otherwise it will insulate most perfectly. It may be mentioned here that for the most delicate possible electrometer, as I found in my experiments on the pocket electrometer, it is useless to expect to find any stability where a liquid surface is pierced. The only method of communicating with the needle is through a silvered quartz fibre. Owing to the insulating quality of a clean quartz fibre, delicate experiments are apt to be disturbed by unintended electrification of the suspension, and this may still remain after means have been employed to prevent it, for mere metallic contact between different metals leaves the surfaces in effect at different potentials, depending on the metals used, and, as I showed, in an idiostatic instrument the disturbance due to platinum and zinc is many hundred times the least that can be detected.

I have sought to reduce this form of error by either or both of two methods. In the first I make the inside of the chamber surrounding the suspension a figure of revolution, the axis being the line of the fibre; in the other, when possible, I make the surfaces of the suspension and of the enclosure one and the same, preferably electro-gilt.

The first method in very small instruments also in the main avoids what can no longer be safely neglected, as it has hitherto nearly always been, viz. gravitational attraction.

There is one more point which may be of some interest. If an unsilvered quartz fibre is threaded through a small hole in a thin metal plate, stretched by a suspended weight, and the hole is then wetted with chloride of zinc and soldered up, the fibre will, after washing off the fused chloride of zinc, pull out, leaving a hole fine and beautifully circular.

It is unnecessary to say more than I have already done, on more than one occasion, on the necessity for making the free space round a suspension in any instrument of extreme delicacy as small as possible and enclosing it by massive metal, itself protected from outside heating and cooling by a non-conducting cover, such as I have in the radio-micrometer; otherwise the convection currents set up in the free space will blow the suspension about, and produce vagaries which might be easily attributed to the fibre or its attachment. The disturbances due to this cause are apt to be much greater than anyone would at first imagine, and the small trouble spent in avoiding them in the manner indicated is well rewarded.

With regard to the manipulation with fine fibres, I have already pointed out that the darkness inside a drawer just pulled out, if the operator is sitting at a table in front of a window with a good light, is such that fine fibres can readily be seen upon it as a background. No velvet or smoked surface or artificial blackness of any kind is comparable with it. On such backgrounds fine fibres are to all intents and purposes invisible. What is in many respects preferable to the dark background, at least in certain operations, is a plain looking-glass lying on the table. Fibres resting upon it become intensely brilliant and visible, provided the eye is so placed as not to see the sky light itself reflected from the mirror. One method of making the fibres very easily visible without influencing their torsion, is to smoke them with burning magnesium or arsenic. I do not suggest arsenic, but I mention it because of the very beautiful effect I once observed, after destroying all life in a small hot-house by burning a large quantity of bengal fire in which orpiment is a considerable constituent. All the spider-webs remained perfect with the spiders in their places as though alive, and the webs were of a dazzling white but perfect in form, undragged by the weight of the white arsenic upon them, thus contrasting strongly with the catenary distorted webs so much admired in frosty weather. It was this observation that suggested the magnesium smoking.

These last few points hardly come directly under the title of this paper, but I thought them worth adding as bearing upon the successful design of apparatus in which the full limit of delicacy and accuracy obtainable by the quartz fibre may be obtained, and upon the practical details of its treatment.

## Discussion.

Mr. Inwards asked if the shellac used to secure the tags was melted or dissolved.

Mr. Blakesley inquired if silvering fibres did not destroy their perfect elasticity.

Dr. Sumpner wished to know if any data as to the relative torsional rigidity of silvered and unsilvered fibres had been obtained, and if the electric resistance of silvered fibres had been determined.

Mr. Watson said silvered fibres had been successfully used in electrometers. As regards their torsion, he had found it differ from day to day, and the resistance varied enormously.

In reply to a question, Prof. Boys described the exact process of soldering the coppered fibre to the tags. As to the torsion of silvered fibres, he would not expect much increase as the film was very thin. He also thought the elasticity would not be destroyed, for silver and gold make very good torsion wires.

## VIII. *A Method of finding the Refractive Index of a Liquid; applicable when the Liquid is not Homogeneous.* *By* T. H. LITTLEWOOD, *M.A.*[*]

### *Apparatus required.*

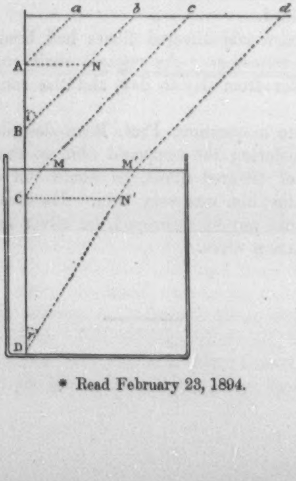
THE chief piece of apparatus required for the method is a telescope with fixed wires in the eyepiece, arranged so as to be capable of motion along a horizontal scale, without changing its inclination to the vertical. The horizontal motion can be measured either by a vernier or by a micrometer-screw.

The liquid whose refractive index is to be determined is placed in a glass vessel about 3 feet away from the telescope, and with its level slightly below that of the telescope.

A scale of glass (or some material not acted on by the liquid) is placed vertically in the liquid and illuminated by monochromatic light. The position of the telescope on the horizontal scale is then taken when observing the various divisions on the vertical scale. From these readings the index of refraction can be ascertained.

*First case.*—When the liquid is homogeneous (fig. 1).

Fig. 1.



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[*] Read February 23, 1894.

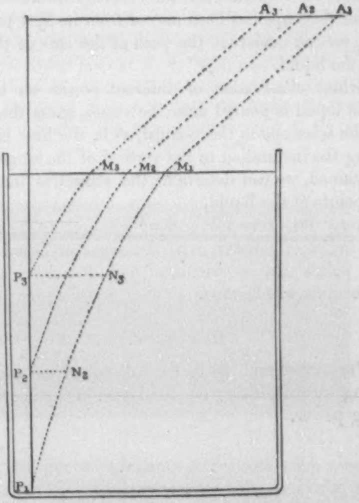
Suppose A, B are two points on the vertical scale out of the liquid ; C, D two points within the liquid. Suppose $a, b, c, d$ are the positions of the telescope on the horizontal scale when observing these points. Then A$a$, B$b$ are parallel ; and if CM$c$, DM$'d$ are the directions of the axis of the pencil of light from C and D, M$c$, M$'d$ are parallel, and also CM, DM$'$ are parallel. Draw AN and CN$'$ parallel to $a\,b\,c\,d$. AN$=ab$, CN$'=cd$.

$$\therefore\ \tan \mathrm{AB}b=\frac{ab}{\mathrm{AB}},\ \text{and}\ \tan \mathrm{CDM}'=\frac{cd}{\mathrm{CD}}.$$

$$\therefore\ \mu=\frac{\sin i}{\sin r}=\frac{\sin \mathrm{AB}b}{\sin \mathrm{CDM}'}=\frac{ab}{cd}\times\sqrt{\frac{cd^2+\mathrm{CD}^2}{ab^2+\mathrm{AB}^2}}.$$

*Second case.*—When the liquid is not homogeneous (fig. 2).

Fig. 2.



The liquid is supposed to have the same density at the same depth, which must be the case if it is at rest. The path of the axis of the pencil of light from any point on the scale which enters the telescope must be a curve.

Suppose $P_1$, $P_2$, $P_3$ various points on the vertical scale, and $A_1$, $A_2$, $A_3$ the corresponding positions of the inclined telescope when observing them. Suppose $M_1$, $M_2$, $M_3$ are the points where the axis of the pencil cuts the surface of the liquid, and draw $P_2N_2$, $P_3N_3$ parallel to the surface. Then it is clear that, since $M_1A_1$, $M_2A_2$, $M_3A_3$ are parallel, $P_2M_2$ is the same curve as $N_2M_1$ moved horizontally, parallel to itself, through the distance $P_2N_2$ or $A_1A_2$. $P_3M_3$ is the same curve as $N_3M_1$ moved through the distance $P_3N_3$ or $A_1A_3$. Similarly for other points.

Hence, by taking a number of points on the vertical scale and finding the corresponding positions of the telescope, and then plotting a curve having the vertical distances from the lowest point for ordinates, and the observed distances through which the telescope has been moved from its first position as abscissæ, we can construct the path of the axis of the pencil through the liquid.

A previous observation of different points on the scale, before the liquid is poured into the vessel, gives the inclination of the telescope to the vertical, as in the first case. By measuring the inclination to the vertical of the tangent to the curve obtained, we can determine the refractive index at the various points of the liquid.

Assuming the curve for a short distance to be a straight line, the index of refraction of the layer of liquid between any two points can be calculated as in the first case, and a similar formula will be true.

## Discussion.

The President said the method described was a novel and interesting way of picking out the layers of liquid of different refracting power.

## IX. *On a new Harmonic Analyser.*

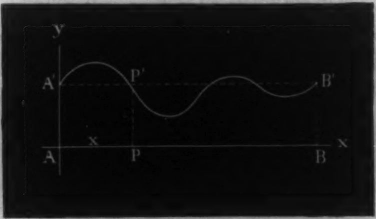
### *By* Prof. O. Henrici, *F.R.S.*[*]

§ 1. According to the theory of Fourier's Series any function $y$ of $x$ can, under certain restrictions, be expanded in a series progressing according to cosines and sines of multiples of $x$.

This function may be represented graphically by a curve, $x$ and $y$ being taken as rectangular co-ordinates, or it may be defined by aid of such a curve.

Anyhow, we shall suppose this curve given, and also that it extends from $x=0$ to $x=c$ (fig. 1). For this interval the curve may be drawn perfectly arbitrary as long as it gives for every $x$ one single finite value of $y$. This implies that if a point moves along the curve the corresponding value of $x$ always increases. The curve may, however, be discontinuous, so that for a particular value of $x$ the ordinate changes suddenly from a value $y_1$ to a value $y_2$, as from C to C′ in fig. 2. There may be any finite number of such discontinuities. For our purposes it is necessary to make the curve continuous by joining the two points C′ and C by a straight line. If the curve represents a periodic phenomenon with period $c$, then the ordinate for $x=c$ will, as a rule, equal the initial ordinate for $x=0$ (as in fig. 1). The curve when

Fig. 1.



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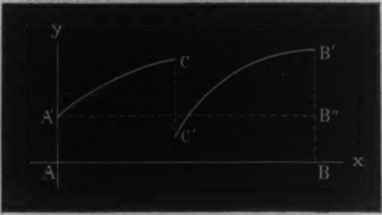
[*] Read March 9, 1894.

repeated along the axis of $x$ will therefore be continuous. Otherwise there will be a discontinuity as at B in fig. 2. In this case also the curve has to be continued from its end point B′ along the last ordinate to a point B″ which has the same ordinate as the initial point A′, so that the line A′ B″ is parallel to the axis of $x$.

Fig. 2.



We can now express the equation to the curve in the form of a Fourier Series,

$$y = \tfrac{1}{2}A_0 + A_1 \cos\theta + A_2 \cos 2\theta + \ldots + A_n \cos n\theta + \ldots$$
$$+ B_1 \sin\theta + B_2 \sin 2\theta + \ldots + B_n \sin n\theta + \ldots$$

where $\theta = \frac{2\pi x}{c}$.

The absolute term $\tfrac{1}{2}A_0$ equals the mean ordinate of the curve, and can therefore be determined by any planimeter. It is the object of the Harmonic Analyser to determine the other coefficients. Their well-known values are

$$A_n = \frac{1}{\pi}\int_0^{2\pi} y \cos n\theta \, d\theta \, ; \quad B_n = \frac{1}{\pi}\int_0^{2\pi} y \sin n\theta \, d\theta .$$

The Analyser is therefore an integrator.

If the paper with the curve be wrapped round a cylinder, the ordinate $y$ falling on the generating lines or edges, the axis of $x$ along a circumference, then the curve will run back in itself and form one continuous line, provided the circumference of the cylinder equals the base $c$. That edge which passes through the initial point A′ of the original curve may be called the zero-edge.

Suppose the cylinder to lie horizontal with the zero-edge at the top, then our angle $\theta$ will be the angle through which the cylinder has to be turned in order to bring that point P to the top which corresponds to any given $x$. Each edge contains one point on the curve, excepting in case of a discontinuity where a finite length of the edge belongs to the curve.

§ 2. The first instrument of this kind was constructed by Lord Kelvin (Proceedings Roy. Soc. vol. xxiv., 1876). Since then several others have been devised. With regard to these I may refer to my article "Ueber Instrumente zur harmonischen Analyse" in the Catalogue prepared by Prof. W. Dyck of Munich for the Mathematical Exhibition which was held last summer in Munich, and also to the descriptions in the Catalogue of the various instruments exhibited.

These instruments differ essentially either in the manner in which the trigonometrical factor is introduced, or in the arrangement by which the actual integration is performed. Lord Kelvin uses for the latter purpose his brother's disk-globe and cylinder integrator, whilst a simple harmonic motion introduces the trigonometrical factor. Sommerfeld and Wiechert * of Königsberg make the cylinder on which the curve is drawn rotate about an axis perpendicular to that of the cylinder, and thus avoid the simple harmonic motion, which is always a drawback, as it introduces a great deal of friction. Both instruments are also large and heavy, practically fixtures in the room where they are used.

§3. Clifford has given a beautiful graphical representation of Fourier's Series, which I knew more fully from personal communication than from the short paper published in vol. v. of the Proceedings of the Lond. Math. Soc.

His result may be stated thus:—"If the curve to be analysed be stretched out in the direction of the $x$ to $n$ times its base without altering the $y$, and then wrapped round a cylinder with circumference $c$ so that it goes $n$ times round, then the orthogonal projection of this curve on that meridian

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* See above Catalogue, p. 274.

plane which passes through the zero-point of the curve will enclose an area which is proportional to the coefficient $B_n$. In the same way $A_n$ is got by aid of a plane perpendicular to the first."

It was this theorem which led me to the construction of an Harmonic Analyser. It can easily be put in the following form. Suppose the cylinder placed with its axis horizontal and the tangent plane to its upper edge drawn. This edge cuts the curve in $n$ points. Let P be one of them. If now the cylinder be turned, and if at the same time the tangent plane be moved in its own plane in a direction perpendicular to the edge of contact, the point P will trace a curve on it. This plane will be the same as Clifford's curve in case the motion of the tangent plane is simply harmonic, completing one period for each rotation of the cylinder. The curve will be completed after $n$ rotations of the cylinder.

The same curve will be traced if the original, unstretched, curve is wrapped (once) round the cylinder, whilst the tangent plane completes $n$ periods of its simple harmonic motions for one revolution of the cylinder.

We thus get in a fixed plane a curve whose area equals, in some unit, the coefficients $A_n$ or $B_n$, and this area can be determined by an ordinary planimeter. The curve, of course, need not be drawn out, as long as the tracer of the planimeter is always at the point P it will describe the curve.

This can easily be realized. A flat board, whose upper surface forms a platform on which the planimeter can rest, is placed by the side of the cylinder so that its upper surface lies in the tangent plane. A straight-edge is fixed above the upper edge of the cylinder. The tracer of the planimeter is pressed against it and made to follow the point P on the curve. After a complete revolution of the cylinder, the planimeter will register a number proportional to the coefficient $A_n$ or $B_n$.

I had an instrument of this kind made early in 1889, but it did not turn out quite as simple as its theory. It gives, of course, only one coefficient at a time, though it would not be difficult to construct it to give more terms if it were not for the mechanism required to produce the simple harmonic motion. This always introduces a certain amount of friction if it is to work accurately. I therefore tried to do away with this, and obtained my object in the manner now to be described.

§ 4. If the definite integrals which determine the coefficients $A_n$ and $B_n$ be integrated by parts, we get for the former

$$n\pi\, A_n = [y \sin n\theta]_0^{2\pi} - \int_0^{2\pi} \sin n\theta\, dy,$$

the limits relating to $\theta$.

If the original curve is continuous, the integrated part vanishes. This is not the case if there is a discontinuity, at least not if $\theta$ is retained as the independent variable.

To prove that in this case also the integrated part can be neglected, let us consider the curve in fig. 2. Let $\theta'$ be the value of $\theta$ for which the discontinuity C C′ occurs, and let $y_1'$ be the ordinate of C, and $y_2'$ that of C′.

The integral with regard to $\theta$ has to be broken up into two, the first going from 0 to $\theta'$, the second from $\theta'$ to $2\pi$. The integrated part, therefore, gives

$$y_1' \sin n\theta' - y_2' \sin n\theta',$$

and this, in general, does not vanish.

The remaining integral has to be taken for the two parts of the curve from A′ to C and from C′ to B′, if the curve is not made continuous. But if the curve is made continuous, we have also to take the integral for the intervals from C to C′, and from B′ to B″. For these $d\theta$ vanishes, but not $dy$. This gives in addition the integrals

$$-\int_{C}^{C'} \sin n\theta\, dy = -\sin n\theta' \int_{C}^{C'} dy = -\sin n\theta'\,(y_2' - y_1');$$

hence just the terms obtained before from the integrated part.

The second integral for the interval B′ B″ vanishes because it is multiplied by $\sin 2n\pi$. In case of the coefficient $B_n$ this is not the case, but then the integrated part also contains more terms which equal it. Hence :—

*If the integration is performed with regard to* y *we get*

$$n\,A_n = \frac{-1}{\pi}\int \sin n\theta\,dy, \qquad n\,B_n = \frac{1}{\pi}\int \cos n\theta\,dy,$$

*both taken over the whole continuous curve from* A′ *to* B″. If the integration be continued from B″ to A′ on the line parallel to the axis of $x$ nothing is added to the integral, because here $dy$ vanishes.

For the Analysers now to be described this extension of the integration should always be made in order to eliminate certain errors of the instrument.

These new integrals are of a very different form from the old ones, and require accordingly a different mechanism. As the tracer of the instrument follows the curve, each $dy$ has to be multiplied by $\sin n\theta$ or $\cos n\theta$. In other words, we have to decompose the $dy$ for each element of the curve into two components at right angles to each other, of which the one makes an angle $\theta$ with the axis of $x$, and then add all components of each kind to get $A_n$ and $B_n$.

Originally I did this by aid of a pair of registering-wheels such as are used in Amsler's well-known planimeter, the axes of the two being at right angles. If such a wheel moves along a straight line of length $p$, making an angle $n\theta$ with its own axis, it will register not $p$ but $p \cos n\theta$, whilst the second wheel at right angles to it gives $p \sin n\theta$.

A model of this instrument was made in 1889.

The curve is wrapped round a horizontal cylinder. Parallel to this a carriage runs on a rail carrying the tracer which moves along the upper edge of the cylinder. It also carries a vertical spindle which has the two registering-wheels attached to it. These roll on a horizontal platform. If, now, this spindle is made to turn through an angle $n\theta$ when the cylinder has turned through an angle $\theta$, and if the tracer is made to follow the curve, then the two registering-wheels will give the coefficients $A_n$ and $B_n$. For the details of the construction I must refer to Prof. Dyck's Catalogue, p. 213.

§ 5. The next improvement is due to Mr. A. Sharp, of the Teaching Staff in the Guilds' Central Technical College. Having used my model, he brought me a design in which the principles explained were realized in a different manner.

Among the alterations introduced one struck me as being of importance. It consisted in an inversion of the motion, the curve being drawn on the drawing-board and the instrument made to move over it whilst the registering-wheels rolled on the paper.

It seemed to me that we had now all the elements needed for a really good instrument, and only wanted a practised instrument-maker to realize it. I therefore called in 1892 on Coradi in Zürich, well known for his planimeters and integrators. He set to work at once and sent me in a short time a drawing of his construction, and it is due to his skill that the instrument has, at last, reached a high degree of perfection. One Analyser has been made for the Guilds' Central Technical College, which I shall describe. But I must mention at once that Herr Coradi has since greatly improved it, so much so that it is now one of the most perfect integrators made.

§ 6. Fig. 3 shows an instrument of Coradi's second design. This will help to explain the first.

There is first of all a solid frame whose base is a long rectangle. It rests with three wheels on the drawing-board. One of these, D, in the middle of the front, serves merely as a support. The other two, E, E, are fixed to the ends of a long axle which runs along the back of the frame. This may be called the "shaft." It is placed parallel to the axis of $x$. The instrument can, therefore, roll over the paper in the direction of the ordinates $y$.

If thus moved through a distance $dy$, the shaft will turn through an angle proportional to $dy$. The shaft carries any required number of short "cylinders." In the figure there is one marked C situated in the middle of the shaft.

Above each of these cylinders is a vertical "spindle" S, whose geometrical axis cuts that of the shaft. In the new instrument each spindle carries one or two disks, $H_3$, $H_4$, in fig. 3; but in the old construction one crown wheel with its teeth pointing upwards, by aid of which the spindle is turned. At the lower end the integrating apparatus proper is attached, which is quite different in the two designs. But before explaining this let me describe how the spindle is turned.

Along the front of the frame runs a carriage W, to which the tracer F is fixed. This can be moved through a distance equal to the base $c$ to which the curve is drawn. To the carriage a silver wire is also attached, which in the new design is stretched along the front of the frame and then by aid of guide-pulleys $l$, $l$ over one of the disks H on top of the spindle S (see fig. 3). By giving the disk H a suitable diameter the spindle can be made to turn $n$ times round, whilst the tracer describes the whole base. In the old instrument the wire only drives an extra spindle in the middle of the frame, which by aid of wheelwork drives all the working spindles. If the tracer on following the curve has reached a point P, then the spindle will have turned through an angle $n\theta$, where $\theta$ corresponds to the $x$ of P.

If, now, the spindle had at its lower end two registering-wheels at right angles to each other rolling on the drawing-paper, we should have in principle my old model (§ 4) with Sharp's inversion. Instead of this Coradi gave each spindle one registering-wheel and made this roll on the cylinder C. This requires for each registering-wheel a separate spindle, hence two for each pair of coefficients $A_n$ and $B_n$. It substitutes, however, the rolling on a smooth surface for that on the rough surface of the paper. The instrument made according to this design for the Guilds' Central Technical College has five such pairs, so that on going once over the curve the first five pairs $A_n$ and $B_n$ are obtained. The extra spindle which is driven by the silver wire contains, however, three extra disks, making four in all. If the wire is stretched over the top disk we get, as stated, the coefficients for $n=1, 2, 3, 4, 5$. The second pulley has half the diameter, so that the spindles turn twice as fast if the wire is stretched round it. Thus in going over the curve a second time we get the new coefficients for $n=6, 8, 10$. The remaining two disks give similarly the coefficients for $n=7$ and $9$ respectively. Hence on going four times over the curve we get ten pairs of coefficients. In most cases the five pairs obtained at once will be amply sufficient.

For the details of the construction I must again refer to Prof. Dyck's Catalogue (*Nachtrag*, p. 34) and only mention a few points. The axis of a registering-wheel lies in the

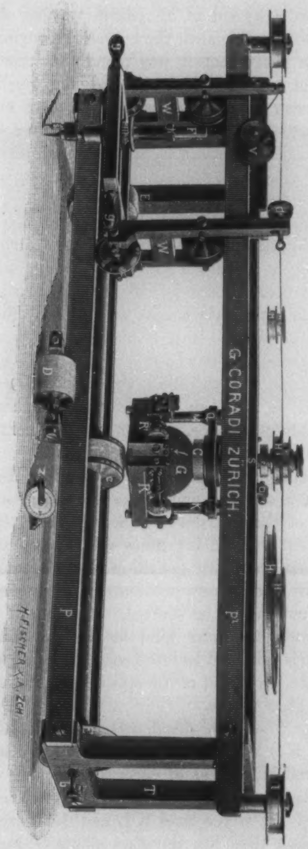


Fig. 3.

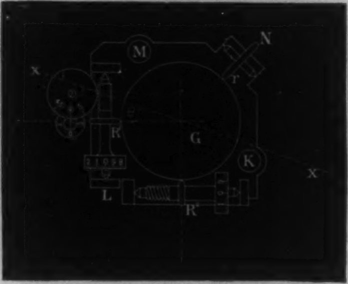
diameter of a horizontal ring which is attached to the lower end of the spindle by aid of an elastic vertical steel plate. This presses the wheel against the cylinder, securing contact. On testing the instrument it was found that this plate was liable to slight torsion which affected the readings. It showed a number of other drawbacks of more or less importance. One is that the registering-wheel not only rolls but also slips. This slipping is absent in the Analyser of Lord Kelvin, who has dwelt strongly on the importance of avoiding it.

There was also a serious difficulty in taking the readings. The instrument registers up to 20 centim. If the zero-point has passed the index which gives the reading, 20 centim. have to be added or subtracted. Every one who has used a planimeter is accustomed to this, and knows how to take account of it, for he can either estimate the area sufficiently to see which correction is necessary, or he can go rapidly over he curve again, watching the zero-point. Neither method is possible with an Analyser which gives a large number of readings at once. The new instrument is therefore constructed to record up to 200 centim.

§ 7. Last summer at the Munich Exhibition Herr Coradi submitted a new arrangement to me to obviate some of the imperfections of the instrument described, and this he has since carried out with an ingenuity which I cannot enough admire. He has practically got rid of all the imperfections of the old Analyser, and has now produced an instrument which, I fancy, leaves nothing to be desired. He himself says it is the best instrument of any kind he has yet made. The chief alteration is this, that he interposes between the registering-wheel at the lower end of the spindle and the cylinder a perfectly free glass sphere.

The "spindle" has now *firmly* attached to its lower end a square frmae K L M N (comp. figs. 3 and 4) by aid of two solid rods K and M, instead of carrying the ring connected by aid of an elastic spring. This frame holds two registering-wheels $R^1$ and $R^2$, whose axes K L and L M are at right angles. Between these lies the glass sphere G, resting with its lowest point on the cylinder belonging to the spindle. A third wheel *r* at N is by aid of a spring pressed against the sphere to secure contact between the latter and the registering-wheels. If, now, the tracer follows the curve this frame will turn with the spindle, the three wheels will carry the sphere with it, which will turn pivot-like on its lowest point. If, as

Fig. 4.



in fig. 4, the plane of one wheel $R^1$ makes with the axis of $x$ an angle $n\theta$, and if in this position the tracer, and with it the whole instrument, is moved through the distance $dy$, the "shaft" will turn proportionally to $dy$. This will set the sphere turning about its horizontal diameter $xx$ parallel to the shaft, and this motion will be communicated to each of the registering-wheels. It will be seen at once, if $q$ denotes the radius of the sphere, the point of contact of the sphere and the wheel $R^1$ is at a distance $q \sin n\theta$ from the axis of the sphere, that therefore the turning communicated to this wheel will be proportional to $dy \sin n\theta$. Similarly the other wheel will turn proportionally to $dy \cos n\theta$. If the tracer moves through the whole curve, these two wheels will therefore register numbers proportional to $A_n$ and $B_n$. The dimensions are so chosen that the readings give $nA_n$ and $nB_n$ in centimetres.

It will be seen that now one spindle does the work of two in the old instrument. There is, further, no slipping of any kind in the integrating apparatus.

Another improvement is that the wheelwork for turning the spindles is done away with. Each spindle is turned directly by the silver wire, and thus any slackness in the wheels is done away with.

It has also been possible to introduce an arrangement to set all spindles to zero after the wire has been tightened.

Lastly, the readings are taken with much greater ease as the registering apparatus is well exposed to the eye.

In order that the instrument may work accurately it is necessary that the point of contact of the sphere with its cylinder should lie in the geometrical axis of the spindle. But it is practically impossible to secure this. This point will therefore describe a small circle on the cylinder and this will turn the sphere about some horizontal diameter, and therefore also the registering-wheels. It is of importance to eliminate the error thus introduced. This is done by bringing the tracer back to the starting-point A on the curve by moving it from B to A (figs. 1, 2) parallel to the axis of $x$. The sphere will hereby repeat the motion which produced the error, but in the opposite sense, and therefore completely cancel it.

§ 8. The first instrument of this kind has been made for Prof. Klein at Göttingen. It contains one spindle, as in fig. 3. Going once over the curves it gives therefore one pair of coefficients. To get more, disks of different diameter have to be used to drive the spindle. Of these six are provided. Since then two further instruments have been finished; one with five spindles, which goes to Moscow, the other, with three spindles, for Prof. Weber in Zürich. The experience gained in the making of the Göttingen instrument has enabled Coradi to introduce a number of small improvements, with the result that the carriage runs in the Moscow instrument, where it has to drive five spindles, as easily as in the one for Göttingen with only one spindle.

He has also introduced a celluloid ring below the sphere, which on being raised presses the sphere against a similar ring above, thus preventing any damage to the integrating apparatus when the instrument is not being used.

*Note.*—At the request of Herr Coradi I add the statement that the idea of the new integrating apparatus, consisting of a sphere with two recording-wheels at right angles to each other, is not his own, but is due to Herr Max Küntzel, of Charlottenhof, near Königshütte in Silesia. Herr Küntzel invented the arrangement for an instrument designed to determine the coordinates of the vertices of a polygon, and submitted his design to Herr Coradi for the construction of such an instrument.

## X. *Harmonic Analyser, giving Direct Readings of the Amplitude and Epoch of the various constituent Simple Harmonic Terms. By* ARCHIBALD SHARP, *B.Sc., Wh.Sc., A.M.I.C.E.**

LET the curve (fig. 1) be that represented by the equation $y=f(x)$, the scale of abscissæ being such that the period is $2\pi$. Suppose a wheel W to roll on the paper (fig. 2),

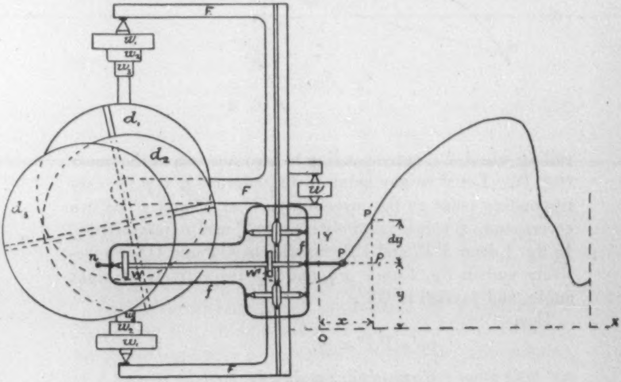


FIG. 1

and to be connected with a tracing-point P (fig. 1) in such a manner that as P moves uniformly in the direction

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* Read April 13, 1894.

OX the axis of the wheel W turns uniformly in a horizontal plane, and the distance rolled through by the wheel during any short interval is equal to the corresponding displacement of the tracer P in the direction OY. If the axis of the rolling wheel W makes one complete turn while the tracing-point P moves over one complete period of the curve (fig. 1), the point of contact of the rolling wheel will describe a curve $Opp'R$ (fig. 2).

Let OY′ (fig. 2) be the initial direction of the plane of the rolling wheel, *i. e.* corresponding to zero abscissa of the tracer (fig. 1). Let P be any point on the curve fig. 1, $p$ the corresponding point on the curve fig. 2. Let P′ and $p'$ be two corresponding points infinitely close to P and $p$ respectively. In fig. 1 draw $P'P_1$ and $PP_1$ parallel to OY and OX respectively, and in fig. 2 draw $p'q$ and $pq$ respectively at right angles and parallel to OY′.

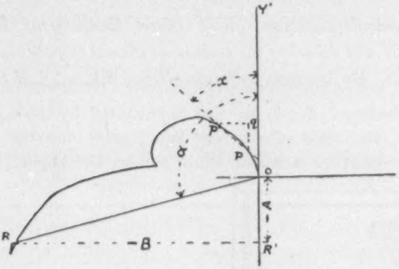

FIG 2

Then

$$pp' = P_1P' = dy,$$

$$p'q = pp' \sin x = \sin x\, dy,$$

$$pq = pp' \cos x = \cos x\, dy.$$

Draw RR′ perpendicular to OY′ (fig. 2), R being the position of $p$ corresponding to $x = 2\pi$. Then

$$\mathrm{RR}' = \Sigma p'q = \int_0^{2\pi} \sin x\, dy,$$

$$\mathrm{OR}' = -\Sigma pq = -\int \cos x\, dy.$$

In the Fourier expansion

$$\left.\begin{aligned} y = f(x) = \mathrm{A}_0 + \mathrm{A}_1 \sin x + \mathrm{A}_2 \sin 2x + \,..\, + \mathrm{A}_n \sin nx + \\ + \mathrm{B}_1 \cos x + \mathrm{B}_2 \cos 2x + \,..\, + \mathrm{B}_n \cos nx + .\,, \end{aligned}\right\} \tag{1}$$

$$\left.\begin{aligned} \mathrm{A}_1 &= \frac{1}{\pi}\int_0^{2\pi} y \sin x\, dx = \frac{1}{\pi}\int \cos x\, dy = -\frac{1}{\pi}\mathrm{OR}' \\ \mathrm{B}_1 &= \frac{1}{\pi}\int_0^{2\pi} y \cos x\, dx = \frac{1}{\pi}\int \sin x\, dy = -\frac{1}{\pi}\mathrm{RR}' \end{aligned}\right\} \quad . \quad . \tag{2}$$

Also $f(x)$ may be expanded in the form

$$\mathrm{A}_0 + \mathrm{C}_1 \sin(x - \alpha_1) + \mathrm{C}_2 \sin(2x - \alpha_2) + \,..\, \mathrm{C}_n \sin(nx - \alpha_n), \tag{3}$$

$\mathrm{A}_n$, $\mathrm{B}_n$, $\mathrm{C}_n$, and $\alpha_n$ being connected by the relations

$$\left.\begin{aligned} \mathrm{A}_n &= \mathrm{C}_n \cos \alpha_n \\ -\mathrm{B}_n &= \mathrm{C}_n \sin \alpha_n \end{aligned}\right\}, \quad . \quad . \quad . \quad . \tag{4a}$$

or

$$\left.\begin{aligned} \mathrm{C}_n^2 &= \mathrm{A}_n^2 + \mathrm{B}_n^2 \\ \tan \alpha &= -\frac{\mathrm{B}}{\mathrm{A}} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \tag{4b}$$

From (2) and (4*b*) it is evident that OR (fig. 2) is equal to $\pi \mathrm{C}_1$, and the angle Y′OR is equal to $\alpha_1$.

If now the axis of the rolling wheel W makes $n$ turns while the tracer P moves over one complete period of the curve (fig. 1), the corresponding values of OR and the angle Y′OR will be $n\pi \mathrm{C}_n$ and $\alpha_n$ respectively.

Various arrangements of mechanism are suggested for connecting the rolling wheel with the tracer so as to satisfy the above conditions; the following seems the most suitable, as it can be adapted for an instrument to give more than one simple harmonic constituent term for one tracing of the curve.

The motion of the rolling wheel relative to the paper is compounded of two simple movements:—(*a*) a pure rolling, the distance rolled being equal to $dy$ the element described by the tracer P; ($b$) a motion of rotation, the point of contact of the wheel with the paper being the centre of rotation, and the angle turned through from the initial line being proportional to $x$ the abscissa of P. The relative motion will, therefore, be the same if the wheel be rolled along a straight line *fixed* in the instrument, while the *paper* is made to turn, the centre of rotation of the paper being the point of contact of the wheel with it which is continually varying in position. Fig. 1 represents diagrammatically the mechanism. The curve to be analysed is drawn on a flat sheet of paper and placed on a drawing-board. The carriage FF, which forms the base of the instrument, is supported by an axle with two equal wheels $w_1$ and a third wheel $w$ which roll on the paper, the direction of motion of the carriage being OX. A disk $d_1$ mounted on a vertical spindle is driven by a pair of bevel wheels by the axle $w_1$ $w_1$. A long key on the upper surface of this disk fits into a groove on the under surface of a disk $d_2$, which is thus free to move in a straight line relative to disk $d_1$. A groove on the upper surface of disk $d_2$ at right angles to that on its lower surface has a key from the lower surface of disk $d_3$ resting in it. Thus the disk $d_3$ always turns with disk $d_1$, although any point on disk $d_3$ may be made the centre of rotation; the three disks being kinematically equivalent to Oldham's coupling for the transmission of motion between two parallel shafts. The keys and grooves would be replaced, in an actual instrument, by wheels and rails, in order to diminish frictional resistance.

The tracing-point P is mounted on a smaller carriage $f$, which is free to run in the direction OY relative to the main carriage F. This smaller carriage carries also the rolling wheel W which rolls on the disk $d_3$. The rolling wheel W should be spherical in form, and of as small diameter as possible, so that its surface of contact with the paper on disk $d_3$ approximates to a point. The friction between wheel W and disk $d_3$ is great enough to prevent any relative sliding. As the tracer P moves over the curve (fig. 1) the point of the wheel W will describe on the disk $d_3$ the curve $Opp'R$ (fig. 2). To ensure that, as the tracer P is moved in the direction OY, the wheel W will *roll* on the disk $d_3$ the same distance and not displace it relative to disk $d_1$, a wheel W′ of the same diameter as W is mounted on the same spindle and rolls on a fixed portion of the carriage FF. If W′ be compelled to roll, W must roll on the disk $d_3$ an equal amount.

The actual shape of the curve O*pp*′R (fig. 2) is of no importance, the initial and final points being all that are required. A needle or pencil *n* may therefore be carried at any convenient part of the carriage *f*, and the initial and final positions O and R marked by it. The direction of the initial line OR will be recorded on the disk $d_3$ by making two marks with the needle *n* as the tracer P moves along the line OY (fig. 1).

The gearing must be such that the disk $d_3$ turns once while the tracer P describes one complete period of the curve. If now pairs of equal wheels $w_2\ w_2$, $w_3\ w_3$, . . . of diameters $\frac{1}{2}$, $\frac{1}{3}$, . . . of $w_1$, be made to roll on flat rails lying on the paper, the values of $c_2$, $\alpha_2$, $c_3$, $\alpha_3$, . . . are obtained in succession, one pair of coefficients for each tracing of the curve.

This instrument has the advantage over any Harmonic Analyser previously designed that it gives directly the quantities—amplitude and epoch—of each simple harmonic term which are required; all other instruments, as far as I am aware, giving the coefficients $A_n$ and $B_n$, from which $C_n$ and $\alpha_n$ are calculated.

It is remarkable that no adjustments have to be made before using the instrument, the initial position of the disk $d_3$ having no influence on the curve O*pp*′R described on it. There is no part of the instrument which demands *excessive* accuracy of construction. The accuracy and delicacy of the instrument depends on the accuracy with which the line OR and angle Y′OR can be measured, and will be quite as great as that with which the original curve fig. 1 is drawn.

In some cases there will be a danger that the disk $d_3$ may not be large enough to contain the complete curve O*pp*′R (fig. 2). If the rolling wheel W is about to roll off the disk, a mark should be made with the needle *n*, and keeping the tracer P in the same position, the disk $d_3$ should be moved by hand into any other convenient position relative to disk $d_1$, a new mark made with the needle, and the movement of the tracer P may then be proceeded with. The final line OR can then be easily built up from its separate parts.

Since writing the above I have designed an inversion of the mechanism described above giving a simple compact instrument, which I may have the pleasure of describing later on.

## DISCUSSION.

The PRESIDENT said a description of Mr. Sharp's Harmonic Analyser, giving direct readings of the amplitude and epoch of the various constituent simple harmonic terms, had been sent in.

This machine requires no adjustments to be made before using. The amplitude is given by the length of a line joining the initial and final portions of the point of contact of a roller with a rotating disc, whilst the epoch is determined by the angle which this line makes with the plane of the roller in its initial position.

Prof. PERRY congratulated Prof. Henrici on the success attained with his analysers. Referring to Planimeters, he said the average error made in working out indicator diagrams with Hine and Robertson's instrument was only about one-third that made with Amsler's. After pointing out the great importance of Fourier's Series to practical men, and especially to electrical engineers, he said that in studying reciprocating motions, such as those of pistons, valve-gears, &c., it was most useful to resolve the motion into its fundamental harmonic motions and its overtones. In this way remarkable differences could be seen between various motions which have the same fundamental, and which are usually considered equivalent. In the 'Electrician' of Feb. 5th, 1892, he had published the numerical work for a given periodic curve developed in Fourier's Series, and he now exhibited a graphical solution done by one of his students, who was probably the first to carry out the late Prof. Clifford's idea of wrapping the curve round a cylinder and projecting it on different planes. Prof. Henrici had, he said, based the construction of his first analyser on Clifford's method, but used the Henrici principle (viz.,

$$\int y \sin \theta dy = \int \cos \theta \, dy,$$

when integrated over a complete period) to explain the later machines. As a matter of fact the first machine, in which the coefficients were determined by the Amsler planimeter carried by a reciprocating tangent plane, was a beautiful example of the Henrici principle, and he, Prof. Perry, saw great possibilities before it. The defects in the first instrument were mechanical, and could be got over by increasing the amplitude of the harmonic motion. Not only was the machine useful for Fourier expansions, but by giving suitable motions to the tangent plane developments of arbitrary functions in spherical harmonics, Bessel's functions, Lame's functions, and other normal forms could be determined. He had designed a machine which, on Prof. Henrici's principle, develops arbitrary functions in Bessels, and hoped to have shown it in working order at the meeting; the Easter holidays had prevented its being finished in time. In this machine the motion is given to the table by a cam and roller, the cam being shaped so that the displacement of the table is $x \times J(x)$ when the shaft turns through an angle proportional to $x$. The revolving cylinder is driven by variable gearing from the cam-shaft. By using curves of other shapes, developments in many normal forms may be obtained; the machine is therefore of general analytical use. An example of development in Bessels worked out arithmetically by two of his students, Messrs. Hunt and Fennell, was given, and the process of performing the integrations by the machine described.

Prof. Boys, speaking of arithmometers, said Prof. Selling's machine had several inconveniences. In the first place, it occupied a large space, and the projecting racks were apt to upset things just behind the machine. Secondly, the result of any operation was indicated by continuous motion, and therefore cannot be read off instantly with certainty. On the other hand, the "Brunsviga" machine was very compact and convenient, the only serious defect being that one cannot carry on figures obtained as the result of one operation to work with again, as was possible in the well-known Colmer machine. As another improvement, he suggested that the two sets of numbers on the wheels showing the result of any operation should be coloured differently, so that it would be easy to see whether multiplication or division had been performed. The labour of operating with large digits could then be considerably reduced with certainty. For example, in multiplying by 2998, instead of 28 $(2+9+9+8)$ turns of the handle, 5 would be sufficient, viz., three in the forward direction and two backward, thus giving $30\overline{02}$. In his opinion logarithm tables were not nearly so convenient for ordinary calculations as this machine.

Mr. A. P. Trotter described how by the use of templates cut to suitable shapes one could obtain true curves from those given by recording voltmeters and similar apparatus.

Mr. Yule said he had recently seen the newest analyser made by Coradi for Prof. Weber, and was present when it was tested by the latter on a simple harmonic curve. It gave excellent results, the errors not amounting to 1 part in 2000. Speaking of the "hatchet" planimeter, he thought that the first one was exhibited by Mr. Goodman at the Institution of Civil Engineers.

Mr. A. Sharp remarked that since last meeting he had designed an inversion of the mechanism in his harmonic analyser, which made it much more practical.

Prof. Henrici, in reply, said the uses of his first machine suggested by Prof. Perry might lead to great developments in this subject. Lord Kelvin had shown that with the sphere and roller integrator, products of two functions, such as $f(x)\, F(x) dx$ could be got. Referring to Prof. Boys's criticism on the Selling arithmometer, he did not consider the difficulty in reading off the result at all serious. Mr. Trotter's method of solving problems by templates might be very useful. Speaking of the "hatchet" planimeter, he said he believed it was first brought out in Denmark; Mr. F. W. Hill, of the City of London School, had sent him a solution of its action. Mr. Sharp, he said, had made a very considerable improvement in his machine, and the elements of this integrator may be useful for other purposes.

## XI. *Remarks on* Prof. Henrici's *Paper made by* Prof. PERRY, *F.R.S., in which he describes a Simple Machine which may be used to develop any Arbitrary Function in Series of Functions of any Normal Forms*[*].

I CONGRATULATE Prof. Henrici, first upon his success in these Analysers, with which I shall presently form a practical acquaintance when the latest of them yet constructed reaches me from Zurich, second on the admirably clear way in which he described them to us.

I have had no experience with the hatchet, that simplest of all planimeters; but with regard to the Robertson-Hyne instrument, which comes to us from America, and which in the size here exhibited is well suited to Indicator-diagram work, I can say that some of my students instituted a careful comparison between it and the Amsler which they use for Indicator diagrams, and they found that the average error with it was about one third of that with the Amsler.

We know that in mathematical physics generally the development of an arbitrary function in a Fourier's Series is often of great importance; but I wish to say that this subject is becoming of greater and greater importance to the practical man—the engineer.

Thus in alternating-electric-current work, all the disturbing, distracting, dangerous troubles are considerably increased when the currents are not simple harmonic functions of the time. With two-phase or three-phase currents, if the amplitudes are not equal, the rotating magnetic field neither remains of constant strength nor has it constant angular velocity; and if there are overtones we have extra fields of changing magnitude, which rotate irregularly at two or more times the speed of the fundamental.

I have long thought that mechanical engineers need such instruments as Prof. Henrici has designed, if only to familiarize them with the ideas of Fourier. It has for some time been my habit, when studying with students any kind of reciprocating motion of a piece of machinery, to resolve the motion into its fundamental harmonic motion and overtones.

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[*] Read April 13, 1894.

For example, if one is studying the forces causing the motion, one ought to keep in mind that the reciprocating motion which (speaking rather vaguely) requires the smallest forces or moments of forces to produce it, is the simple harmonic motion. The accelerating forces due to an octave are four times as great as for a fundamental of the same amplitude. The motion of the piston of a steam-engine is, with sufficient exactness for practical calculations, a fundamental of amplitude $r$ and an octave of amplitude $\frac{r^2}{4l}$, where $r$ is the length of the crank and $l$ the length of connecting-rod.

A special graphical method of study may be discovered and employed for any special motion; but for applicability to reciprocating motions in general I know of nothing to compare with the method of study which is based on finding the fundamental motion and one or more overtones.

Again, the difference between one kind of slide-valve motion and another may be exceedingly great, practically, and yet the theories found in books show no difference at all. Indeed, the complete mathematical methods of study are too troublesome, but the mathematics of link motions and radial valve-gears become very simple when we consider, not merely the fundamental simple harmonic motion, which is all that is usually studied, but the octave, which is found to help or hurt in the various forms.

I was first attracted to this subject when studying the beautiful but little-known valve-motion invented long ago by Sir F. Bramwell, in which the only overtone is three times the fundamental.

Given any function completely, we can by a numerical method, and with as much accuracy as we please, develop it in Fourier's Series. In the 'Electrician' of Feb. 5th, 1892, I published the numerical work of one example calculating from 23 ordinates. In the sheet which I here exhibit one of my students, Mr. Fox, has done the same work by a graphical method. Probably he is the very first to carry out the idea of the late Prof. Clifford by descriptive geometry*. That is,

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* *Note added May 29th.*—The descriptive geometry method is fairly quick, and may be made as accurate as one pleases, but of course it cannot compare in quickness with the Henrici Analyser.

It is obvious that by properly shaping one's cylinder, wrapping the we have imagined the curve to be wrapped round the cylinder, and it was surprising to find how rapidly its projections could be drawn upon the two planes and their areas obtained by the planimeter. We then imagined the curve to be wrapped twice round and the projections drawn and their areas taken. I wish I had time to dwell upon the interesting problems that arose during the work, for example as to whether the area was to be taken as positive or negative. However many loops such a figure may possess, the well-known rule for autotomic plane circuits (Thomson and Tait's 'Elements,' §445) is really attended to by the planimeter. The direction of motion of the tracer must be that in which $x$ increases on the real curve. I here give the results :—

The values of the arbitrary function to be analysed were really calculated from

$$y=10+5\sin\left(\frac{2\pi}{c}x+30^\circ\right)-\sin\left(\frac{4\pi}{c}x-60^\circ\right).$$

The result obtained numerically and published in the 'Electrician,' using 23 ordinates, was

$$y=9\cdot966+5\cdot039\sin\left(\frac{2\pi}{c}x+29^\circ\cdot9\right)-1\cdot053\sin\left(\frac{4\pi}{c}x-55^\circ\cdot3\right).$$

The result now obtained graphically is

$$y=10\cdot01+5\cdot0096\sin\left(\frac{2\pi}{c}x+30^\circ\cdot38\right)-1\cdot0099\sin\left(\frac{4\pi}{c}x-59^\circ\cdot22\right).$$

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curve round it, and then finding the area of it, projected on a plane parallel to the axis, one may develop an arbitrary function in a series of any normal forms. Thus if $Q(x)$ is any tabulated function of $x$, and $y$ is the arbitrary function of $x$, and we wish to find the integral $\int_0^a y\,.\,Q(x)\,.\,dx$, the shape of the curve which must be used instead of a circle in the Clifford construction is easy to find. It must be such that the cosine of the angle which the short length $\delta x$ of the curve makes with the trace of the plane on which the projection is to take place shall be proportional to $Q(x)$, and several easy methods of drawing the curve or a series of such curves may be found. Once found, there is no more difficulty in developing any new arbitrary function in any series of normal forms than Mr. Fox found with his Fourier Series. A series of curves will be needed for a development in Zonal Harmonics, but only one curve will be needed for the Zeroth Bessels. These curves, or shapes of sections of cylinders, I am now proceeding to draw on a sufficiently large scale for exact work.

It is curious that Prof. Henrici should have based the construction of his first or 1889 instrument on the beautiful idea of the late Prof. Clifford, and not on what I call the Henrici principle. He gives the Henrici principle to explain the later instruments, and does not seem to see that his first instrument is the most beautiful example of its application. I take the Henrici principle to be that

$$\int y \,.\, \sin\theta \,.\, d\theta = \int \cos\theta \,.\, dy,$$

the integrations being for a whole period. Well, in his first instrument, whilst its tracer moves through the distance $dy$, the ordinarily fixed part of the planimeter now has a displacement $\cos\theta$, and this is the same as if in the ordinary use of the instrument a curve is being traced whose ordinate is $\cos\theta$.

It is only on the assumption that the Henrici principle applies to his first instrument, that I venture to say that the following analyser is on the Henrici principle. We have at present to develop functions in sines and cosines, spherical harmonics and Bessel functions, because we know that when we have effected such developments we can convert them at once into the solutions of certain physical problems. As time goes on we shall require developments in many other normal forms. I propose to describe a machine which will effect any such development. I mean, that my machine will evaluate the integral $\int_0^a f(x) \,.\, \mathrm{Q}(x) \,.\, dx$, where $y=f(x)$ is an arbitrary function of $x$ and $\mathrm{Q}(x)$ is any tabulated function. Following Henrici, we convert the required integral into

$$\Big[_0^a f(x) \,.\, \mathrm{H}(x)\Big] - \int \mathrm{H}(x) \,.\, dy,$$

where $\mathrm{H}(x)$ is the integral of $\mathrm{Q}(x)$ and may be tabulated as $\mathrm{Q}(x)$ is tabulated. Now in many cases the part between the square brackets is zero, but this is of little consequence in comparison with the fact that the part $\int \mathrm{H}(x) \,.\, dy$ may be evaluated by a machine somewhat like Prof. Henrici's first or 1889 instrument. I have worked with this 1889 instrument, and I am not disposed to think it so inaccurate as its inventor thinks it. Its defects are really defects of mechanical construction ; for example, the amplitude of the simple harmonic motion of its table is very much too small.

I have already put my machine in hand and hoped to exhibit it here to-day in working order, but unfortunately the Easter holidays have prevented it being finished in time. It is arranged to develop an arbitrary function in Bessels of the zeroth order, or rather Fourier cylindric functions. Thus it is required to determine the constants $A_1$, $A_2$, &c., in

$$f(r)=A_1J_0(\mu_1r)+A_2J_0(\mu_2r)+\&c., \quad . \quad . \quad . \quad . \quad (1)$$

where $\mu_1, \mu_2$, &c. are the successive roots of some such equation

as $$J_0(\mu a)=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or $$\mu aJ_1(\mu a)-\lambda J_0(\mu a)=0, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $\lambda$ has a given value.

It is well known that

$$A_s=M\int_0^a rf(r) \,.\, J_0(\mu_sr) \,.\, dr,$$

where $M=2/a^2\ [J_1(\mu_sa)]^2$, if $\mu_1, \mu_2$, &c. are the roots of (2), and

$M=2\mu^2_s/(\lambda^2+\mu^2_sa^2)\,[J_0(\mu_sa)]^2$, if $\mu_1$, $\mu_2$, &c. are the roots of (3).

In every case the practical difficulty consists in finding the integral. I exhibit to the Society an easy example of such an analysis worked out numerically (I suppose that such a thing has never been done before) by two of my students, Mr. H. F. Hunt and Mr. W. Fennell.

It will be seen that the work is rather tedious. It was made more tedious by their having found it necessary to calculate numbers and tabulate them in a handy form, interpolating between the numbers given in Lommel by the use of his formula. Before this work was finished we discovered Dr. Meissel's elaborate tables, from which the remainder of our handy four-figure tables is merely copied. These handy tables of $J_0(x)$ and $J_1(x)$ are at the service of the Society; they would occupy just four pages of the Journal. We have found them of practical value, but I do not know whether they are of such general value that they ought to be printed.

It is well known that $\int_0^x xJ_0(x) \,.\, dx=xJ_1(x)$, and hence if we write $\phi(r)$ for $\mu r \mathrm{J}_1(\mu r)$, and $y$ for our arbitrary function $f(r)$, the required integral $\int_0^a rf(r) \, . \, \mathrm{J}_0(\mu r) \, . \, dr$ is

$$\frac{1}{\mu^2}\int_0^a y \, . \, \frac{d\phi(r)}{dr} dr = \Big[_0^a \frac{1}{\mu^2} f(r)\phi(r) \Big] - \frac{1}{\mu^2}\int \phi(r) \, . \, dy.$$

The part between the square brackets is usually 0, but however that may be, we see that we can evaluate the integral by the machine. A curve is drawn representing $f(r)$ from $r=0$ to $r=a$ on a sheet of paper which is wrapped round a roller. $a$ need not be equal to the whole circumference of the roller and the scale of $r$ is unimportant. Of course the ordinate $y$ or $f(r)$ lies parallel to the axis of the roller. It is the measurement of $y$ in inches which my instrument analyses, as my planimeter is graduated in square inches. A table whose upper surface is in a plane tangential to the roller carries the usually fixed part and rolling wheel of an Amsler planimeter. On turning through an angle $\theta$ a handle which drives a shaft on which a properly shaped cam is keyed, the table is displaced in its own plane towards the roller, through the distance $x \, \mathrm{J}_1(x)$, $\theta$ being proportional to $x$, and at the same time the roller is driven so that the paper moves circumferentially through a distance proportional to $x$. For this particular kind of problem a few different but definite trains of gearing might be used to connect the handle and the roller, but for general purposes I would prefer variable friction gearing to give any relative speeds that may be necessary. In my model now being constructed I am using two disks, one of which rests on the other at a point which may be altered, radially. As in Prof. Henrici's instrument, the tracing-point of the planimeter is held against a straight edge, so that it can only move along the tangent-line of roller and table whilst following the curve on the roller.

If $\mu$ is a root of $\mathrm{J}_0(\mu a)=0$ as in the well-known drum-head problem, $a$ being the radius of the drum-head,—in the first operation to find $\mathrm{A}_1$, the gearing must be adjusted so that when the whole curve on the roller passes under the tracing-point of the planimeter, a graduated circle on the shaft turned by the handle indicates that it has turned through an angle proportional to 2·405, which is the first value of $x$ which satisfies $J_0(x)=0$.

It is advisable to have a pointer and a scale to indicate exactly the displacement of the table, so as to test the accuracy with which the cam performs its duties. Of course, when the graduated-circle indication is 2·405, the displacement of the table is to be $2{\cdot}405\ J_1(2{\cdot}405)$ or $-1{\cdot}249$ inches. The area recorded on the planimeter in square inches must now be multiplied by $2(2{\cdot}405)^2/a^4[J_1(2{\cdot}405)]^2$, and the answer is $A_1$.

To find $A_2$: change the gearing so that when the whole roller-curve passes under the tracing-point of the planimeter, the graduated circle indicates 5·5201, and check the error of the cam by noting that the displacement indication ought now to be $5{\cdot}5201\ J_1(5{\cdot}5201)$ or 1·878 inches. The area recorded by the planimeter in square inches must now be multiplied by $2(5{\cdot}5201)^2/a^4[J_1(5{\cdot}5201)]^2$. If variable frictional gearing is used, it is important that the roller should be placed on roller bearings of small resistance.

To develop an arbitrary function in Bessels of any other order, or in Fourier's Series, or in zonal harmonics, or in series of functions of any other normal forms, we have only to replace the cam by one of another shape; so that this one simple machine is suited to quite general analytical use.

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## XII. *On the Mechanism of Electrical Conduction.*—Part I. *Conduction in Metals.* *By* Charles V. Burton, *D.Sc.*[*]

1. The view of electrical conduction which it is here my object to explain receives general support from more than one consideration; for it leads to the conclusion that deviations from Ohm's Law must be quite inappreciable in the case of metallic conductors, and it goes far to explain, I think, why metals are so much less opaque than their ordinary conductivities would lead us to infer. But it is not

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[*] Read April 27, 1894.

alone on such considerations that we have to rely, for, as it seems to me, the main conclusions are capable of exact demonstration ; and accordingly it would appear most convenient to commence with a few simple theorems, seeking afterwards to account for known phenomena by means of our definite results.

### 2. THEOREM I.

*In a region containing matter, there may be (and probably always are) some parts which are perfect insulators and some parts which are perfect conductors ; but there can be no parts whose conductivity is finite—unless every finitely conductive portion is enclosed by a perfectly conductive envelope.*

Before proceeding to the proof of this theorem, it may be remarked that the presence of the last clause in no way modifies any application of our result, since the space within a perfectly conductive envelope is completely shielded from the influence of external charges, currents, or magnets. In the present state of science, indeed, such words appear necessary to the completeness of demonstration, but they do not need to be considered in any of our deductions from the theorem, and for my own part I am persuaded that in reality there is nothing corresponding to the possibility which they suggest.

Consider now the case of any body whatever, at any temperature other than absolute zero. We know that electromagnetic radiations will spread out into the ether surrounding the body, and we must suppose that the intermolecular spaces within the body are also traversed by electromagnetic disturbances. Let us suppose then, for a moment, that in the molecules of the body there are some finitely conductive portions which are *not* enclosed in perfectly conductive envelopes. The electromagnetic disturbances will give rise to currents of conduction in these portions, and accordingly energy will be degraded into a form which is *not heat*, since it consists, not in the motion or relative positions of molecules or appreciable parts of molecules, or in electromagnetic disturbances of the intervening ether, but in something *much more fine-grained*. We shall thus have *a continual degradation* *of heat into energy of a lower form*; for the electromagnetic "damping" of the finitely conductive bodies involves a continual drain on the energy of internal radiation, and hence indirectly on the energy of the molecules, so that heat will be automatically dissipated in the interior of the body. This process, in which the radiative molecules are continually imparting to the ether more energy than they receive in return, may be compared to the surface cooling of an isolated body which radiates towards colder surroundings.

Even if we suppose the finitely conductive bodies to be extremely small and their conductivity to be either extremely small or extremely great, it is not hard to see that the rate of absorption of heat must be tremendous; and when we consider (for example) the effect which even a very slow absorption, continued for millions of years, would have had on the temperature of our planet, we must admit that the absence of that dissipation of heat implied in the denial of Theorem I. has been established with an exactitude almost unparalleled. Thus the theorem is established.

3. In connexion with this result we are reminded that Poisson's theory of dielectrics requires the molecules of insulating substances to possess some conductive portions, though whether the conductivity of such portions is finite or infinite is of no moment in electrostatics. On the other hand, both Ampère's theory of magnetism and Weber's theory of diamagnetism suppose the existence of *perfectly conductive particles*, and are thus strongly supported by our result.

In discussing Weber's theory of diamagnetism, Maxwell* points out that the currents excited in a perfectly conductive body by any external cause are entirely confined to the surface of the body. Thus the *perfectly conductive bodies* in Theorem I. may be replaced by *perfectly conductive surfaces*, without altering any of our conclusions; but it would be hard to decide whether a perfectly conductive geometrical surface is or is not a physical possibility without knowing more of electromagnetism—not to speak of ordinary matter.

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* 'Electricity and Magnetism,' 2nd ed. vol. ii. § 840.

## 4. THEOREM II.

*In metals, and in other non-electrolytes whose conductivity is finite, the transmission of currents must be effected by the intermittent contact of perfectly conductive particles.*

For if there were not these intermittent contacts, any given two of the conductive particles would be either permanently in contact with one another, or permanently out of contact, and there would be only two cases to consider. If throughout the substance there extended continuous chains of (perfectly) conductive particles in contact with one another, the substance as a whole would be a perfect conductor; while in the absence of such chains of particles, the substance would be a perfect non-conductor. Finite conductivity can only exist when the contacts are intermittent.

5. An immediate corollary is

## THEOREM III.

*If we suppose that in a substance at the absolute zero of temperature there is no relative motion amongst the molecules or amongst their appreciable parts, it follows that every substance at this temperature must have either infinite specific resistance (which need not imply infinite dielectric strength), or infinite conductivity.*

For the denial of relative motion involves the denial of that intermittence of contact which in Theorem II. was shown to be necessary to finite conductivity.

This conclusion is in accordance with the experiments of Dewar and Fleming* on the resistance of pure *unalloyed* metals at very low temperatures. In the case of all the pure metals examined by these authors (platinum, gold, palladium, silver, copper, aluminium, iron, nickel, tin, magnesium, zinc, cadmium, lead, and thallium), the temperature-resistance curves are almost straight lines, and these, being produced, would pass very nearly through the point whose coordinates are zero temperature and zero resistance.

The same was *not* found to hold good for the temperature-resistance curves for alloys; but if these curves could be pursued far enough by experiment, they must be found, I think, to terminate at the origin of coordinates, like those of the pure metals.

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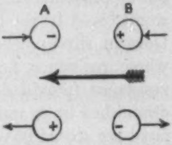
* Phil. Mag. Sept. 1893, p. 271.

## 6. Dissipation of Energy in a Conductor conveying a Current.

In fig. 1 let A and B be two perfectly conductive particles (whether molecules or parts of the same or of different molecules we need not consider), and let them be approaching one another. Suppose also that there is an applied E.M.F. acting from right to left (as indicated by the large arrow). Then, generally speaking, A will be negatively electrified, owing to a previous encounter with some particle farther to the left, and for a similar reason B will in general be positively electrified. When A and B collide, the usual effect is to leave A on the whole positively electrified, and B negatively electrified.

Fig. 1.



Remembering that the conductivity of A and B is perfect, let us consider what transformations of energy are effected by movements and collisions of this kind. Before the collision, A being negatively electrified is urged towards the right by the applied E.M.F., while B being positively electrified is urged towards the left: that is, A and B are urged *together*, and are gaining kinetic energy at the expense of the source of applied E.M.F. After the collision, the electrifications are, generally speaking, reversed, so that A and B are now being urged apart by the applied E.M.F., and continue to gain kinetic energy as before. Further, when particles such as A and B come into collision, so as to cause a re-adjustment of their electrifications, and also when they are in motion between two collisions, electromagnetic disturbances will be produced in the intermolecular ether; but since all the conductive particles are perfectly conductive, no electromagnetic energy can penetrate within them. Thus the energy expended by the source of E.M.F. which maintains a steady current through a conductor is converted partly into additional energy of the molecules, and partly into electromagnetic disturbances of the intervening ether: that is, *the dissipated energy takes the form of heat*, as we know from experiment.

## 7. OHM'S LAW.

In the case of a metal wire (especially one at a bright red heat), Ohm's Law has been verified with great exactitude, the results of the experiments designed by Maxwell and carried out by Chrystal being summed up by the latter in the following words [*]:—"If we have a conductor [of iron, platinum, or German silver] whose section is a square centimetre, and whose resistance for infinitely small currents is an ohm, its resistance (provided the temperature is kept the same) is not diminished by so much as the $1/10^{12}$ part when a current of a farad per second passes through it."

Now when a current is conveyed through a substance by intermittent contacts amongst a number of perfectly conductive particles, the effective conductivity depends firstly on the properties of the intermolecular medium, and secondly on the size, form, distribution, and movements of the particles themselves. In order that the resistance of the conductor may be sensibly constant—in order, that is, that the current transmitted may be sensibly proportional to the impressed E.M.F.—two conditions must evidently be satisfied:—

(i.) For such values of impressed electromotive intensity as exist in the intermolecular spaces (say about ·003 volt per cm.) the relation between electromotive intensity and electric displacement must be sensibly linear.

(ii.) The forces which the particles of the substance experience owing to the impressed E.M.F. must be very small in comparison with the ordinary intermolecular forces, so that during the time of a single molecular excursion the motion of no particle is appreciably influenced by the presence of the E.M.F. If we suppose that in the conducting substance we can maintain a steady distribution of temperature which is independent of the current flowing through, this second condition implies that the particles of the substance under the steady distribution may be regarded as a system of perfect conductors, whose coordinates are explicitly given functions of the time, and are sensibly unalterable by an E.M.F. impressed upon the system from without. This condition, combined with (i.), will evidently give us Ohm's Law.

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[*] B. A. Report, 1876, p. 61 of Reports

Now the forces actually present and tending to modify the heat-movements are of two kinds: electromagnetic and electrostatic.

(a) *Electromagnetic Forces.*—The passage of a current through a conductor gives rise to a magnetic field, which may or may not appreciably affect the conductivity. The thin iron wire used by Prof. Chrystal was ·0021 cm. in radius, and the greatest value of the magnetic force due to a current of 1 ampere per square centimetre of cross section would be in absolute measure about ·0013 (at the surface of the wire), the square of the greatest magnetic force being thus about ·0000017. The average value of (magnetic force)$^2$ over the cross section of the wire would be half of this, or ·00000085; that is, about ·0000039 of the square of the terrestrial "total force" in these parts.

Now Lord Kelvin found * that the change of resistance due to *transverse* magnetization of an iron plate by a powerful Ruhmkorff electromagnet was only just decided enough to be distinctly appreciated with the apparatus which he employed, and we may therefore conclude that in Prof. Chrystal's iron wire no perceptible change of resistance could have been produced by the magnetic field of the current. In other metals the effect must be still more insignificant.

On the other hand, the *longitudinal* magnetization of an iron wire perceptibly increases its electrical resistance, so that it would be easy to construct a simple conductor whose resistance at a given temperature was a function of the current-strength. For let a flat bobbin be wound with iron wire, so that each turn has the form of an elongated rectangle, and then let a further quantity of iron wire be wound in a similar circuit embracing the first. Finally let the coils be joined in series with a source of E.M.F. When a current is sent through the circuit, each coil will magnetize longitudinally some parts of the wire of the other coil, and so, for a given temperature of the wire, the resistance will increase with the current.

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* Phil. Trans. 1856, especially pp. 747–749.

(b) *Electrostatic Forces.*—Let us attempt to calculate the electrostatic energy per cubic centimetre which a mass of iron possesses in virtue of a current flowing through it with a "density" of 1 ampere per cm.$^2$ To do this we must assume some value for the specific inductive capacity of iron *, and in order to take a sufficiently unfavourable view of the question, let us assume the value to be as high as 20. Taking the specific resistance of iron in electromagnetic measure to be 10,000, and remembering that 1 ampere $= \cdot 1$ absolute unit, we have for the electromotive intensity 1000 electromagnetic units of potential per cm., *i. e.* $1000 \div (3 \times 10^{10})$ electrostatic units per cm. Hence the electrostatic energy per c. c. due to the impressed E.M.F.

$$= \frac{20}{8\pi(3 \times 10^7)^2} \text{ ergs ;}$$

while to calculate the *thermal* energy per c. c. at "a bright red heat"—the temperature of the iron in the British Association experiments—we have:—

Temperature above absolute zero (say) $= 727 + 273$
$= 1000$ Cent. degrees,
Density of iron . . . . . . . . $= 7 \cdot 8$,
Specific heat . . . . . . . . . $= \cdot 113$,
One gram-water-degree of heat . $= 42 \times 10^6$ ergs.

Thus (roughly speaking) the thermal energy per c. c. reckoned from absolute zero

$$= 1000 \times 7 \cdot 8 \times \cdot 113 \times 42 \times 10^6 \text{ ergs.}$$

A comparison of these results gives

$$\frac{\text{electrostatic energy due to impressed E.M.F.}}{\text{thermal energy}} = \frac{1}{4 \times 10^{22}}$$

---

* In electrostatic measurements conductors appear to have an infinite specific inductive capacity; but here, where the potential really varies from point to point through the metal, it is the true (finite) specific inductive capacity which concerns us.

only, even on our assumption that the specific inductive capacity of iron in electrostatic measure is as high as 20. If we suppose that half the thermal energy is potential and half kinetic, then the electrostatic energy would be $1 \div (2 \times 10^{22})$ of the thermal kinetic energy ; that is, would be equal to the additional energy required to increase the existing velocity of every particle by one part in $2 \times 10^{22}$. When due account is taken of these results it is not surprising to find that in iron at a given temperature the specific resistance for a current-density of one ampere per cm.$^2$ differs from the specific resistance for an infinitesimal current-density by less than one part in $10^{12}$.

The same remarks apply with even greater force to platinum and German silver, the other metals examined by Prof. Chrystal, since the *magnetic* influence of the current on the resistances of these metals must be far less than even in the case of iron.

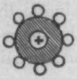
From considerations similar to these, we should expect in all true conducting substances (even in those having marked magnetic properties) to find a sensibly linear relation connecting current-density with electromotive intensity in the neighbourhood of each point.

## 8. Contact E.M.F. and the Peltier Effect.

It will now appear that, by assuming in each molecule a mere arrangement of conducting and non-conducting parts, we may realize what is at all events a working model of contact E.M.F. and of the Peltier effect ; and even should our model serve no other purpose, it directs our attention to a possibility which seems so far to have been overlooked, and which must, indeed, continue to be overlooked so long as each metal is regarded as homogeneous. As it not my object to state with becoming vagueness an hypothesis as to the nature of Peltier's phenomenon, but rather to picture as clearly as possible a mechanism whose principle may perhaps be suggestive of the truth, I shall assume for the molecules such a structure and distribution as appear most favourable to simplicity of treatment.

Suppose, then, that in one of the metals with which we have to deal, each molecule is of the form indicated in fig. 2: a central perfectly conductive body, charged (say) positively, being completely surrounded by an insulating layer, and this again being partially (though not completely) enclosed by a number of perfectly conductive particles. It will be convenient to suppose that in each molecule these outer particles are all electrically connected with one another. When two such molecules come into collision, the outer particles of the one may not in general be reduced to the same potential as those of the other, for the electrical oscillations occasioned by the contact may not have time to subside into insignificance before the encounter is ended. But the general tendency of a collision between two molecules will be towards an equalization of the potentials of the outer particles, and the average values of potentials and charges amongst any considerable number of molecules will be the same as if, during each molecular encounter, this equalization has been completely effected.

Fig. 2.



It will here be convenient to introduce the term "conduction-potential," and as we proceed the following definitions will be found useful:—

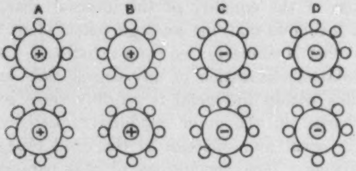
*The conduction-potential of a molecule* is the potential (or average potential) of its outer conductive particles.

*The conduction-potential at a point* within a metallic body is the average conduction-potential of the molecules in the neighbourhood of that point.

Let us now turn to the case of a considerable mass of metal, made up entirely of such molecules as that sketched in fig. 2; every molecule having the same structure and the same internal charge. Let us suppose also that the mass of metal is at the same temperature and in the same physical condition throughout, so that the average distance between adjacent molecules is the same in the neighbourhood of each point. If the metallic body is subjected to electrostatic induction, it is easy to see that no electric influence from without can penetrate far beyond the surface; for the outer particles of the superficial molecules, owing to their intermittent contacts with one another, will screen the interior of the metal as a network of continuous wires might do, and at a depth of a very few molecules beneath the surface the screening will be practically complete. Thus any charge communicated to the conductor will be confined entirely to the superficial layers of molecules; and it follows that if between any two points well within the metal there were a difference of average conduction-potential, there would be a general flow of electrification from the higher towards the lower potential. The average conduction-potential within the metal does not therefore vary from point to point, and account being taken of the equality of the internal charges of the molecules, it follows that the average potential of the intermolecular ether is similarly free from variation. This implies that the total electrification of any considerable assemblage of molecules within the metal is sensibly zero; so that the average charge on the outer conductive particles of each molecule is equal and opposite to the fixed charge on the central particle. The conclusions of this paragraph have been necessarily confined to molecules not too near the surface; for although the general tendency of an encounter between two molecules is always to equalize their conduction-potentials, these potentials change somewhat after the molecules have become separated, and near the free surface of the body the change will be systematically greater for the molecule which moves outwards after collision than for that which moves inwards.

We may now try to realize what will happen when contact takes place between two metals whose molecules are constructed on the general plan of fig. 2, while those of the one metal are not identical with those of the other. The most simple and intelligible view will be obtained by supposing the molecule of the one metal to have a positively charged central particle, while the molecule of the other has its central particle negatively charged (fig. 3). Consider what would occur if we could start from a condition in which each of the *border* molecules, A, B, C, D, &c., had *on the whole* no charge; a condition, that is, in which the outer particles of each molecule had a charge equal and opposite to the fixed charge of the central particle. (We have already seen that this is true for the *average* molecule *within* a homogeneous metallic mass.) Now when B and C come into collision, it is evident that the outer particles of B will lose some of their negative electrification, while the outer particles of C will lose some of their positive; and thus we see that when the distribution of conduction-potential has become steady, such border particles as B or C will have on their outer particles a (negative or positive) charge *less* than the (positive or negative) fixed central charge, and to a smaller extent the same will be true of particles (such as A, D, &c.) more remote from the border. But when the settled condition has been reached, the passage (say) of B backwards and forwards between A and C will not change the distribution of charges amongst the molecules; and the condition that no change of the kind shall take place is that when two molecules are in a position to collide their conduction-potentials shall be equal. Now when B approaches C (which has on the whole a negative charge) its potential is lowered, and when B returns towards A its potential rises again, *so that if* B *in its backward and forward motion is not to act as a systematic carrier of electrification between* A *and* C, *the conduction-potential of* A *must be higher than that of* C. Similarly, by considering C as moving backwards and forwards between B and D, we can see that B must have a higher conduction-potential than D.

Fig. 3.



This gives us *a contact-difference of conduction-potential*.

If we suppose our analysis to become a trifle less penetrating, such molecules as B (and to a less extent A, &c.) will appear to be positively electrified, C, D, &c. will appear to be negatively electrified, and molecules farther removed from the border will appear unelectrified. With still less microscopical vision, we shall find the conduction-potential constant from point to point throughout the mass of metal on either side of the surface of separation; but as we approach that surface from the left, the conduction-potential begins to diminish, changing very rapidly by a finite amount as we pass through the boundary.

We now come to a theorem which is certainly true for our model, and which seems to me as certainly true for any mechanism which could be devised to represent the Peltier effect; but for the sake of avoiding questions of too controversial a character, the statement may be made in this conditional form:

### THEOREM IV.

*In our model, the contact-difference of* conduction-*potential between two metals is equal to the coefficient of the Peltier effect.* For when a molecule at the junction is moving backwards and forwards between places of different potentials, provided no current flows through the junction, as much electrification is carried from the lower to the higher potential as from the higher to the lower, and on the whole there is no transformation of electric energy into heat, or *vice versâ.* But when a current flows across the junction from the metal of lower to that of higher conduction-potential, the molecules at the junction are persistently carrying more electrification from the lower to the higher potential than they bring back with them on their return, and thus on the whole the movements of the molecules at the junction are systematically opposed by electrostatic forces. It is evident from elementary considerations that the quantity of electricity which has crossed the junction, multiplied by the step of (conduction-) potential up which it has passed, is the measure of the total work done by the molecules against electrostatic forces, and is therefore the measure of the heat absorbed. Similarly, when a current has been flowing from the metal of higher to that of lower conduction-potential, the quantity of electricity which has crossed the junction, multiplied by the (negative) step of conduction-potential, is the measure of the (negative) heat absorbed; that is, numerically, of the heat given out. Hence, in our model, the coefficient of the Peltier effect is equal to the contact-difference of conduction-potential.

Again, generally speaking, we may expect a difference of conduction-potential between a hotter and a colder portion of the same metal, owing to the increase of molecular distances which rise of temperature produces; and it is evident *that (on our model) the specific heat of electricity for any metal is equal to the rise of conduction-potential for one degree rise of temperature.*

9. From these results we pass on to

### THEOREM V.

*For any pair of metals at the absolute zero of temperature, the Peltier effect vanishes.*

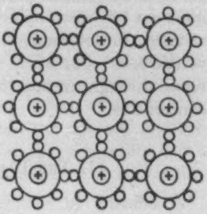
This is evidently true for our model, for when the molecules are all reduced to relative rest, and there is permanent instead of intermittent contact amongst their outer particles, the conduction-potential will be uniform throughout both metals, and at the junction there will be no Peltier effect. But whatever view we take of the nature of the phenomenon, the proposition is necessarily true. For if the Peltier effect had a finite value for a pair of metals at the absolute zero of temperature, we could cause an absorption of heat by sending a current through the junction in the proper direction; and this is impossible, since there is no heat to be absorbed.

## 10. VOLTA E.M.F.'s.

We must now consider a possibility suggested by our model, and referred to in the opening sentence of §8. It is not difficult to see that, with molecules constructed on the plan of fig. 2, even when all measurements are made *in vacuo*, the conduction-potential of a mass of metal is not in general the same as the potential estimated by work done on an external charged body, or by electrification induced on a second mass of metal insulated from the first,—potential measured in the latter way being called for distinction the *induction-potential.*

We may realize this most easily by considering the case of two metals in contact at the absolute zero of temperature, for

Fig. 4.



then, in accordance with the last section, the Peltier effect at the junction vanishes, and the *conduction*-potential is the same throughout both metals; while on the other hand the difference of *induction*-potential may be finite. Let fig. 4 represent diagrammatically a very large number of molecules which are at rest with their outer conductive particles in electrical contact throughout. Let the fixed central charge of each molecule be positive. Then, if the outer conductive particles of each molecule formed a complete envelope around the central charge, the *induction*-potential of the metal would be identical with its *conduction*-potential, and the same as if the fixed central charges did not exist. But since we suppose the fixed charge in each molecule to be *incompletely* screened by the outer particles, it follows that at external points in the immediate neighbourhood of the metallic body the potential is raised above the conduction-potential by the fixed central charges. If these last were negative instead of positive, the potential just outside the metallic mass would be lower than the conduction-potential; and we may suppose that at any given temperature (such as the absolute zero with which we are dealing) the difference between the conduction-potential of a metallic body and the potential just outside the body depends upon the nature of the metal. Thus, even *in vacuo*, if two metals at the absolute zero of temperature be connected together so as to have the same conduction-potential, their induction-potentials may be different; and in general, whatever the temperature of the metals in contact, we may expect an inequality between difference of *conduction*-potential and the difference of *induction*-potential.

Before attempting to devise a model of Peltier's phenomenon and of electromotive forces of contact, I had held the opinion—in common, I believe, with the majority of disputants in the contact-force controversy—that the inductive measurement of potential-differences in a sufficiently perfect vacuum must conclusively decide the points at issue. But if in reality there should be, as the model suggests, a difference between conduction-potentials and induction-potentials, we must not rely upon inductive experiments, even in a perfect vacuum, to determine the seats of electromotive force in a voltaic cell. For when we are dealing with the flow of currents through metals, it is the *conduction*-potential which concerns us.

## 11. THE TRANSPARENCY OF METALS.

A difficulty in connexion with this subject is stated by Maxwell in the following well-known passage*:—"Gold, silver, and platinum are good conductors, and yet, when formed into very thin plates, they allow light to pass through them. From experiments which I have made on a piece of gold-leaf, the resistance of which was determined by Mr. Hockin, it appears that its transparency is very much greater than is consistent with our theory, unless we suppose that there is less loss of energy when the electromotive forces are reversed for every semi-vibration of light than when they act for sensible times, as in our ordinary experiments." Now we have seen that conduction is not a perfectly continuous phenomenon, but is due to innumerable encounters among perfectly conductive particles, and without entering upon any calculations (which indeed would be a difficult matter) we can see that there are, broadly speaking, two reasons why the opacity of metals is so much smaller than is indicated by Maxwell's analysis: these are, heterogeneity of structure and intermittence of contact.

To realize the influence of heterogeneity of structure without the complication of intermittent contacts, take the case of a metal at the absolute zero of temperature. We have then virtually to deal with a network of perfect conductors, constituting a body which as a whole has perfect conductivity, and of which even an excessively thin film would be an effectual barrier to electromagnetic waves, provided that the wave-length were great enough to justify us in treating the metal as homogeneous. But if we consider an extreme case, where the wave-length of the disturbance is negligible in comparison with the dimensions of a single conductive particle, a very thin layer of the metal will be far from absolutely opaque. For the conditions of the problem will then be the same as if we had ordinary luminous radiations obstructed by an agglomeration of perfectly reflecting bodies of appreciable size. Of course these extreme conditions are not realized in the case of the light transmitted by a metallic film; but if we may suppose that the diameter of a conductive particle is not quite negligible in comparison with a wave-length of light, it is clearly to be expected that very thin layers of the metal will fall short of that absolute opacity which in this case would follow from the assumption of homogeneity.

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* 'Electricity and Magnetism,' 2nd ed. vol. ii. § 800. Wien (Wiedemann's *Annalen*, xxxv. pp. 41–62) found a silver film to have only such an opacity as would be deduced from about 1/440 of its actual conductivity.

When we pass to the consideration of metals at ordinary temperatures, the conductivity for steady currents is finite; but for electromagnetic waves of short period we cannot even treat the metal as an agglomeration of finitely conductive particles continuously in contact with one another. It is evident that the shorter we make the period of the electromagnetic disturbance in comparison with the average intercollisionary period of a (perfectly) conductive particle, the more nearly do the particles act as if permanently insulated from one another, and the less efficiently does the metal perform the functions of an electromagnetic screen.

Further considerations might be added concerning the average interchange of electrification between colliding particles when the electromotive intensity tending to produce such interchange is very rapidly alternating; but enough has been said to show that the opacity of conductors must be far less for luminous radiations than for electromagnetic disturbances of long period, and we may fairly expect, I think, that the transparency of metals is to be explained without attributing any new properties to the electromagnetic field.

The second part of this paper will deal with electrolytic conduction and disruptive discharge.

### *Note added April 30th.*

In the course of the discussion Prof. S. P. Thompson objected to the arrangement of molecules in rectangular order, and he further suggested that the arguments might only be applicable in two dimensions. I had omitted to mention that the figures were intended to be sectional views of three-dimensional models, while the rectangular arrangement of molecules was merely adopted to save prolixity in the descriptions, and was so far from being essential to the investigation that the case of irregularly distributed coordinates and velocities was constantly before my mind. Another point raised by Prof. Thompson must also be considered here: in § 6 it does not necessarily follow that two conductive particles oppositely charged like A and B (fig. 1), approaching one another and subject to the influence of an external E.M.F. acting from right to left, would have the signs of their respective electrifications reversed by a *momentary* contact; in some encounters the readjustment of electrifications might even be in the opposite sense; but I think we may safely admit that *in the long run* the effect of innumerable collisions amongst such conducting particles as A and B will be to transfer electrification in the direction of the impressed E.M.F.

Prof. Rücker recalled a difficulty, which Lord Kelvin pointed out some time ago, in connexion with the collisions between molecules. If we suppose the molecules to be constituted like little pieces of elastic solid, every collision will cause some additional amount of translational energy to be converted into energy of vibration, and heat-energy will be continually running down into energy of shriller and shriller vibrations, that is, into energy of a lower form. In the foregoing pages, electrical contact between particles is supposed to occur during a collision, and Prof. Rücker remarked that the method suggested for avoiding an electromagnetic degradation of energy left untouched the corresponding mechanical difficulty. I have made some attempt to deal with this mechanical question in a previous paper*, where it was shown (§§ 10, 11) that, granted the fundamental assumption and an infinite propagation-velocity for gravitational stress, we may construct an atom having a finite number of freedoms. But in whatever way mechanical degradation of energy were eliminated, the difficulty of electromagnetic degradation would also have to be met, and without the doctrine laid down in Theorem I. there appeared to me to be no means of escape. Without making any assumption as to the constitution of a molecule or the nature of a collision, we may admit that in any body not absolutely cold there are particles in relative motion, so that two neighbouring particles are sometimes nearer together and sometimes farther apart. To realize the intermittence of contact required by Theorem II., we have only to suppose that when (but not until) the proximity of two particles has reached a certain limit electrification is capable of passing freely from one to the other.

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* "A Theory concerning the Constitution of Matter," Proc. Phys. Soc. vol. xi. pp. 285, 286.

The question of perfect or imperfect conductivity in the ultimate particles of bodies must be of importance in relation to the constitution of matter and its connexion with the ether; and whether or not the demonstrations above can be generally accepted as conclusive, the subject is certainly one which will repay further investigation.

### Discussion.

Prof. S. P. Thompson thought the paper had an important bearing on the kinetic theory of solids. He saw no reason why Ohm's law should be proved, for he regarded it as a definition.

The President said the author represented all actions as being due to collisions, thereby introducing the same difficulties as were felt in the kinetic theory of gases, viz., that collisions would give rise to mechanical oscillations in the molecules of shriller and shriller pitch. Prof. J. J. Thomson had recently given an explanation of electrical phenomena by vortex filaments.

After some remarks on the visibility of molecules by Mr. Hovenden,

Dr. Burton, in reply to Prof. Thompson, said Ohm's law, when expressed as

$$\frac{E}{C} = a\ constant,$$

was really a law, and not a mere definition.

## XIII. *The Minimum Temperature of Visibility.* *By* P. L. Gray, *B.Sc., Assoc. R.C.S., Lecturer in Physics, Mason College, Birmingham*[*].

The title of this paper is, for convenience, somewhat elliptical. Fully, it should be "The Minimum Temperature at which a Strip of Platinum, either bright or lamp-blacked, becomes visible in the dark."

Apparently no exact work has been done on the point since that of Draper ("On the Production of Light by Heat," Phil. Mag. 1847, xxx. p. 345), who used a somewhat similar method to that described in this paper. This work seems to be generally little known, vague statements, usually without authority, being given when the subject is referred to at all. It only fell under the present writer's notice after the observations, detailed below, had been completed.

Draper looked at a small strip of platinum, only $\frac{1}{20}$ inch wide, in a dark room, gradually heating the metal by an electric current until it became visible, and estimating its temperature from its linear expansion, measured by a magnifying-lever method. Taking a mean coefficient of expansion, from Dulong and Petit's results, with a lengthening of $\frac{1}{222}$, he arrives at a temperature of 525° C. This is obviously too high, as no account is taken of the increase of the coefficient with temperature. Taking the most recent result[†] for platinum,

$$\alpha=10^{-9}(8901+1{\cdot}21t),$$

or

$$\frac{dl}{dt}=10^{-9}(8901+1{\cdot}21t);$$

and integrating, we have

$$l_t-l_0=10^{-9}\times 8901t+10^{-9}\times 1{\cdot}21\frac{t^2}{2},$$

or

$$\frac{1}{222}={\cdot}0045045= \quad ,, \quad ,, \quad ,,$$

whence $t=490°$ C.

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[*] Read April 13, 1894.

[†] J. R. Benoit, *Travaux et Mémoires du Bureau International des Poids et Mesures*, vi. 1888, p. 90.

As this formula was only tested experimentally up to about 73° C., it is most likely that another term, in $t^2$, should be added, which would somewhat reduce this value, and thus produce a satisfactory agreement between Draper's result and the maximum obtained by myself.

In the same paper Draper arrives at the conclusion that *all solid bodies become visible at the same temperature*; a conclusion which is fully borne out by the observations given below, as to the equality of temperatures in the case of bare and lamp-blacked platinum.

Draper's value being, as shown above, somewhat doubtful, the point seems worthy of more exact experiment, both from a physical and a physiological point of view; and as I had, in beginning a series of investigations on Radiation, a means of keeping a platinum surface at any desired temperature, I made a number of observations on the subject, while waiting for other apparatus for use with which the platinum strip was primarily intended.

The instrument in question is Wilson and Gray's modified form of Joly's Meldometer, and is described in their paper, "Experimental Investigations on the Effective Temperature of the Sun," read before the Royal Society on March 15th, and shortly to be published*. It consists essentially of a strip of very thin platinum, about 10 centim. long, 1 centim. broad, and $\frac{1}{50}$ millim. thick. The plane of the strip is vertical.

It can be heated by an electric current, and its linear expansion is indicated by an optical method, by which an alteration in temperature of 1° can easily be noticed. The method of calibration is described in Joly's paper†, and in that already mentioned, so that it is unnecessary to do more than briefly refer to it here. Minute fragments of substances of known melting-points are placed on the strip and watched through a microscope, while the temperature is very slowly and cautiously raised until, in any case, melting is seen to take place, when the position of the spot of light which indicates the expansion of the strip is noted. In these experiments the substances used were $K_2NO_3$ (339°), AgCl (451°), KBr

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* Phil. Trans. 1894.

† Proc. R. I. A. vol. ii. 3rd series, 1891–92, p. 38.

(699°), and gold (1041°)[*]. From these observations a curve showing the relation between temperature and scale-readings is obtained. One point may, however, be mentioned, viz. as to the difference of temperature between the middle of the strip and its surface. Joly says[†] that the difference is probably measured by hundredths of a degree only. The following figures will show the correctness of this assumption.

At a temperature of about 500° C., amount of energy lost per second per square centimetre $= \cdot 3$ calorie.

Thickness of section $= \frac{1}{50}$ millim. $= \cdot 002$ centim.

$\therefore$ Half „ „ $=$ $\cdot 001$ „

Flow of heat $= \dfrac{k\theta}{d}$, where $k =$ conductivity $(= \cdot 2)$, and $\theta =$ the difference of temperature required, at the ends of the distance $d$ $(= \cdot 001$ centim.),

$$\therefore \ \cdot 3 = \frac{\cdot 2\theta}{\cdot 001}, \quad \text{whence } \theta = 0^\circ{\cdot}0015.$$

The loss of energy per unit area was obtained by a voltmeter-and-ammeter method, which is to be further developed for the Radiation experiments. All the figures are approximate, the smallness of the resulting difference (about $\frac{1}{1000}$ ° C.) showing that there is here no need for any high degree of accuracy.

With the surface of the platinum lampblacked the case is different; but even here an approximate calculation shows that there is still less than 1° difference between the platinum and the surface of the carbon. In a typical case the following results were found:—

Thickness of layer $= \cdot 00033$ centim. This was determined from a knowledge of the specific gravity of the lampblack.

Conductivity $= \cdot 0002$. This is the value given by Everett for powdered carbon, and is probably *less* than the correct value for the lampblack; but the two must be of about the same order of magnitude.

Loss of heat per unit area at 500° C. $= \cdot 5$ calorie per second;

$$\therefore \ \cdot 5 = \frac{\cdot 0002\,\theta}{\cdot 00033}; \quad \therefore \ \theta = 0^\circ{\cdot}8.$$

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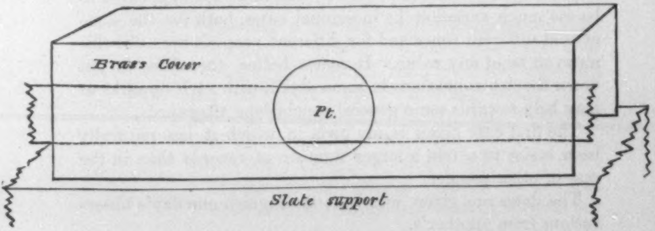
[*] See the same two papers already quoted.

[†] Proc. R. I. A. vol. ii. 3rd series, 1891–92, p. 49.

### *Method of Making the Experiments.*

The first requisite was to get the strip in a perfectly dark enclosure, within which both eyes could be directed towards it without strain. To this end the apparatus was enclosed in a wooden box (blackened within), one end of which was replaced by a black velvet cloth, under which the observer placed his head, and which he could gather round his neck and under his chin so that not a ray of light could penetrate the enclosure. The box was about 48 centim. long, 30 broad, and 22 high, and ordinarily the eyes, in making an observation, would be about 30 centim. from the strip. The other end of the box was provided with a hinged shutter, which was lifted immediately after an observation had been made, for the purpose of noting the temperature of the strip.

The strip itself was further protected from draughts &c. by means of a piece of brass, bent twice at right angles, and resting on the slate block below the strip, as in the calibration experiments; thus (natural size) :—



The angular dimensions of the surface of platinum, as seen in any experiment, were therefore :—

Apparent length = 3° 49′ approximately ;
" width = 1° 54′ "

so that the apparent area subtended was about 36 times that of the full moon.

The current by which the strip was heated ran through a variable carbon resistance, the handle of which was within convenient reach of the observer as he sat with his head under the black cloth. He could thus alter the temperature of the platinum until it was on the very verge of invisibility, a very small fraction of a turn being then sufficient to produce utter darkness where before the area of faint light had been. A contact-breaker was also within convenient reach, so that the current could be broken or made at pleasure, and the objective reality of the faint luminosity at the limiting-point thus demonstrated. When he was satisfied that the limiting-point had been reached the hinged end of the box was opened, a beam of light sent to the mirror connected with the strip, and the deflexion, giving the temperature, read on the scale. The possible error in the estimation of the absolute value of the temperature may be taken as certainly not more than 2°.

### *Discussion of the Results.*

My first idea, in putting down final results, was to take the mean of a large number of observations as expressing the required minimum temperature; but there soon appeared to be too much variation in individual cases, both for the same eyes at different times and for different people's eyes, for this mean to be of any value. It seems better, therefore, to put down the determinations in some detail, with such remarks as may help towards some general conclusions afterwards.

The first case given is my own, in which it has naturally been easier to obtain a larger number of records than in the case of other people.

The dates are given merely to distinguish one day's observations from another's.

The letter B after any temperature signifies that the surface was lampblacked in that experiment; otherwise it was bare, and in its ordinary condition of polish.

The details of the observations are as follows:—

Feb. 10th. 451°, 460°, 460°, 444°, 447°, 448°. Observations made in the morning, without any special preparation as to resting the eyes.

„ 14th. 427°, 422°, 422°. Evening.

„ 15th. 437° (B), 432° (B), 427° (B), 427°, 427°. Evening.

Feb. 16th. 422°, 418°, 421°, 419° (B), 419° (B). Evening; 2nd observation after two minutes in complete darkness.

„ 19th. 410°, 410°. Evening.

„ 22nd. 409°, 409°, 408°. Evening.

After these observations more attention was paid to the time of day and the state of preparation of the eyes.

Feb. 26th. 401°, 397°; 388°, 394°, 384°; 398°, 403°. Evening. Between 2nd and 3rd observations, 11 minutes were passed in perfect darkness; after the 5th, 10 minutes in writing under a bright incandescent lamp.

Before the next set, 16 minutes with eyes shut in nearly dark room :—

383°, 392°, 392° (B), 409° (B), 409° (B), 416°, 417°, 409°.

„ 27th. 470°, 464°, 461°, 463°. Morning (bright).

413°, 414°; 392°, 400°, 400°; 410°. Evening; 3rd observation after half an hour with eyes shut. Several more observations were made, showing a regular fall of temperature after resting the eyes in the dark, and a rise after reading &c., the limits being about 390° and 410°.

„ 28th. 455°, 447°, 447°; 459°. Morning (dull).

„ „ 453°; 417°, 415°, 419°. Afternoon; 4 minutes in darkness after 1st observation.

„ „ 407°; 389°, 389°; 404°, 399°; 392, 392°, 393°. 16 minutes in darkness between 1st and 2nd observations; 12 minutes' reading between 3rd and 4th, and again a few minutes' rest after the 5th.

Observations on two succeeding days gave readings varying from 470° in the morning to 385° in the evening, the influence of rest in darkness being always plainly marked.

To test if the intervals of rest noted above were sufficient to bring the eyes to their extreme state of sensitiveness, some observations were made at 3 A.M., after I had been asleep in a dark room for 3 hours. The readings then obtained were 373°, 386°, showing a slightly greater sensitiveness than that in any previous experiment; the small difference probably indicates that the eyes were very near their extreme limit, and that no longer rest would give a lower reading.

Before going on to the general conclusions to be drawn from these results, the values are given obtained by other observers, who (with the exception of two) were either members of the staff, or students, of Mason College. They are probably not equally trustworthy, and in general no particular preparation was gone through by the observer.

Usually the first observation in each case showed a higher temperature than the second and succeeding ones. This was to be expected, since the time spent in darkness during the first experiment prepares the eye to a certain extent for the second. The results obtained are as follows:—

| | | |
|---|---|---|
| Case A. | Mean temperature . . | 432° C. |
| ,, B. | ,, ,, . . | 422 |
| ,, C. | ,, ,, . . | 436 |
| ,, D. | ,, ,, . . | 409 |
| ,, E. | ,, ,, . . | 428 |
| ,, F. | ,, ,, . . | 438 |
| ,, I. | ,, ,, . . | 426 |
| ,, J. | ,, ,, . . | 440 |

All the above were taken either in the morning or early in the afternoon.

Case H. Mean temperature . . 408°.

In this case the room was darkish.

| | | |
|---|---|---|
| Case G. | Evening . . . . . . | 388° |
| | Morning . . . . . . | 435° |
| | Evening . . . . . . | 380°–385° |

The last observation was made after 17 minutes had been spent by the observer with his eyes shut in the nearly dark laboratory.

## *General Conclusions.*

(1) *That the minimum temperature of visibility is the same for a bright polished metallic surface as for one covered with lampblack*, although the intensity of the radiation in the two cases may be different.

This result may at first be, to some, unexpected, but a little consideration will show that it might have been, *à priori*, anticipated. For probably temperature governs the highest wave-length from a radiating body, and wave-length governs visibility, at least after an extremely small intensity of radiation has been passed *.

(2) *That the visible limit at the red end of the spectrum varies greatly for a normal eye, according to its state of preparation*; *i.e.* according to the intensity of the light in which the observer has been before making the observation.

I take my own eyes as normal; they have been tested in the Anthropometrical Laboratory at S. Kensington, and roughly by Captain Abney's method; and in the figures given above the results are supported by those obtained by the other "cases," none of whom † are known to have abnormal sight.

Speaking generally, we may say that a bright light diminishes the sensitiveness of the eye to radiation of low frequency; that darkness increases it. Or that, as a rule, the eye is less sensitive in the morning than at night.

(3) *That for the less sensitive condition, the minimum temperature of visibility for the surface of a solid is about* 470° C., *but that this may be much reduced by even a few minutes in a dark room.*

(4) *That at night, a surface at a temperature of* 410° *is visible, and that by resting the eyes in complete darkness, this may be reduced to as low as* 370° *nearly, below which apparently one cannot go*, since 10 minutes' rest appears to be almost as efficacious as 3 hours'.

(5) *That different people's eyes (of no special or known departure from normality) differ somewhat in their "minimum temperature of visibility," but probably not to any great extent, if tested under the same conditions as to preparation, &c.*

Case G was a somewhat curious one; the observer was the one exception among those I tried whose red colour-perception is perhaps not quite normal. He arrived at the lowest temperature in the evening without any long rest in the darkness, and, as is seen above, 17 minutes in perfect darkness produced no alteration; yet, in the morning, he went up to about the usual figure, so that what I had hoped to find an abnormal case turned out approximately ordinary.

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* Langley, "Energy and Vision," Phil. Mag. xxvii. (1889), shows that the amount of energy sufficient to excite vision is immensely less than that radiating from the strip in these experiments, at least in the low-red wave-lengths.

† With the possible exception of Case G.

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The loss of distinct *colour* at the low temperatures is very striking; the appearance to myself, and to most of the observers, has absolutely nothing of red in it, but is like a white mist—the nearest comparison I can make.

In the *morning* observations, however, when the strip disappeared at from 460° to 470°, the last appearance was distinctly reddish; and this agrees with one observation noted at night, when after getting the visibility critical-point at about 390° C., the temperature was raised until one could declare for certain that the light looked red: it was then found to be 449°.

Of course, in all the observations, the luminous area was most distinctly seen by somewhat averting the gaze from it: generally I found it best to look in the direction of either far upper corner of the enclosure.

As already mentioned, most of the observers pronounced the appearance at the critical-point to be that of a "whitish mist;" one, however, thought he saw a slight "lilac tinge" in it; and "Case G" declared it to be decidedly yellow, which is interesting, because to him a red mark on white paper (such as a pip on a card belonging to one of the red suits of a pack) appears yellow, by artificial light at night.

In one experiment a plate of glass, $\frac{1}{8}$ inch thick, and in another a layer of water, $\frac{1}{2}$ inch thick, were inserted between the strip and the eye, without making the slightest difference in the phenomenon; showing (1) that the point where these substances begin to be more or less opaque to infra-red radiation had not been reached; (2) that the small difference in intensity produced by their insertion had no appreciable effect. This last conclusion is far more strongly borne out by the equality of temperature in the case of the bare metallic and the black surfaces, and indicates that in all the cases it was *wave-length*, and not *intensity*, which was determinative of visibility, so disposing of the possible objection that the difference between "morning" and "evening" might be due merely to the state of enlargement of the pupil of the eye, which would naturally be more contracted at the one time than at the other, thus affecting the total amount of radiation falling on the retina. Also, if such an objection were valid, it would imply that fatigue of the muscles of the iris produced a relatively enormous "time-lag" in following changes of luminous intensity, which we know does not exist.

There seems, in fact, to be little doubt that the difference is due to the retina itself becoming sensitive to long waves after rest, which were incapable of affecting it when it was in some way fatigued by exposure to the ordinary bright light of day.

The next and obvious step is to find the respective wave-lengths corresponding to the different temperatures. This point, however, and others, cannot be determined without some additions to the present apparatus, and will form the subject of a future paper.

## DISCUSSION.

Mr. **BLAKESLEY** inquired if the author had tried condensing the light from the strip. As to colourlessness, he observed that the parts of the retina active in oblique vision were less sensitive to colour than the central portions.

Dr. **BURTON** remarked that in the experiments the presence of light and not colour was being observed. When illumination was faint, as in twilight or moonlight, it was very difficult to distinguish colours. In the solar spectrum one did not see any whitish termination at the red end.

Mr. **ELDER** said that Captain Abney had shown that all colours appear grey when of small intensity.

The **President** thought the question as to whether visibility depends on wave-length or on energy was an important one ; probably a minimum amount of energy was essential. At such low temperatures the emission curves of the different wave-lengths may not have become sufficiently separated to be distinguished.

Mr. **Gray**, in reply, said Prof. Langley had shown that a minimum, but very small, amount of energy was necessary to vision in all parts of the spectrum.

# PROCEEDINGS

OF

# THE PHYSICAL SOCIETY

# OF LONDON.

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APRIL 1894.

## XIV. *On the Design and Winding of Alternate-Current Electromagnets.* By SILVANUS P. THOMPSON, *D.Sc., F.R.S., and* MILES WALKER[*].

1. IN designing electromagnets for use with alternate currents various considerations enter which do not enter into the design of electromagnets for use with continuous currents. Chief of these considerations are the self-inductive action of the windings, and the frequency of the alternation of the current.

As with continuous-current electromagnets, so with alternate-current magnets, the degree to which magnetization is carried in the magnetic circuit of given configuration depends upon the number of ampere-turns of the excitation. The methods of predetermining the number needed to produce any desired degree of magnetization are too well known to need any reference. Our present aim is to show how to determine the winding which will, under given circumstances as to frequency, voltage, &c., produce any desired number of ampere-turns.

2. As a preliminary, however, it is needful to touch upon the point whether an electromagnet (properly laminated, it is understood) will give an equal pull, when excited with an equal number of ampere-turns of alternating current.

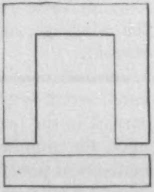
[*] Read April 27, 1894.

Since the pull of an electromagnet upon its armature depends upon the normal tension along the magnetic field integrated over the area of the pole-face, and this tension is proportional to the square of the intensity of the magnetic flux, then, if this flux were proportional to the number of ampere-turns of excitation (as would be the case if the permeability were constant), the pull would be proportional to the square of the number of ampere-turns. Now the amperemeters for alternate currents operate upon principles that cause them to indicate the square root of the mean square values of the current. Hence it follows that, if permeability were constant, the pull should be proportional to the square of the current, whether the current be continuous or alternating. But since, with an alternating current of the same nominal value as a continuous current, the magnetism is carried at each period to a point considerably higher than with the continuous current, and since also at the higher degrees of magnetization the permeability is lower, it follows that the pull of the electromagnet when excited by alternate currents ought to be slightly less if the excitation is so great as to carry the magnetization into the regions commonly spoken of as approaching saturation. The pull ought to be independent of the frequency of the alternation provided this exceeds a certain minimum.

Experiments made show that these views are justified in practice.

An electromagnet of the form shown in fig. 1 was made up of iron stampings about 0·5 millim. thick.

Fig. 1.



The principal dimensions were as follows :—

| | |
|---|---|
| Mean length of limbs and yoke . | 38 cms. |
| Breadth of limb . . . . . . . | 3·1 cms. |
| Gross thickness of limb . . . | 2·54 cms. |
| Nett thickness of limb . . . . | 2·1 cms. |
| Nett cross section of limb . . . | 6·5 sq. cms. |
| Width between limbs . . . . | 6·3 cms. |
| Total length of armature . . . | 12·7 cms. |

The stampings of the armature were of the same thickness, number, and breadth as those of the electromagnet. In the succeeding experiments the electromagnet was wound with 163 turns of copper wire 2·03 millim. in diameter, and the armature was separated from the pole-faces by a distance-piece of wood 0·952 centim. thick.

TABLE showing Pull and Different Frequencies with various Currents.

| Exciting Current. Amperes. | Mean lines per sq. centimetre. | Pull, in grammes, with Continuous Current. | Pull, in grammes, with Alternate Current. |
|---|---|---|---|
| A. *At a frequency* | *of* 30 *periods per* | *second.* | |
| 8 | 2300 | 280 | 280 |
| 12·5 | 3600 | 820 | 820 |
| B. *At a frequency* | *of* 60 *periods per* | *second.* | |
| 8 | 2300 | 280 | 280 |
| 10·2 | 2900 | 530 | 550 |
| C. *At a frequency* | *of* 90 *periods per* | *second.* | |
| 4 | 800 | 60 | 60 |
| 4·2 | 1100 | 100 | 100 |
| 10·2 | 2900 | 530 | 530 |
| 21 | 5600 | 2400 | 2200 |
| D. *At a frequency* | *of* 120 *periods per* | *second.* | |
| 13·2 | 3900 | 900 | 900 |
| 21 | 5600 | 2400 | 2200 |

These experiments show that the pull was exactly the same when the intensity of the flux did not exceed 4000 lines per square centimetre. At higher degrees of magnetization the pull with alternate currents is slightly less.

It may be remarked that at higher intensities and with higher frequencies, eddy-currents, if any are present, will produce, for an equal flow of exciting current, a greater demagnetizing action, and therefore lessen the pull. On the other hand, if the current is supplied at a constant (alternating) voltage, eddy currents do not decrease the magnetization but cause more current to flow in proportion.

Another experiment was made with a solenoidal electromagnet with a laminated U-form plunger belonging to a Brush alternate-current arc-lamp. This plunger with attached mechanism weighed about 820 grammes, and was arranged to be drawn up into position by a current of 10 amperes. This plunger was loaded with various weights and the current required to raise it was measured, with the following results:—

| Total weight. Grammes. | Continuous Current. Amperes. | Alternate Current. Virtual Amperes. |
|---|---|---|
| 820 | 10 | 10 |
| 933 | 17·2 | 18 |
| 1039 | 18·2 | 19·5 |
| 1276 | 25 | 26·5 |
| 1601 | 31 | 33 |
| 1728 | 36 | 40 |

3. When alternate currents are supplied at a given voltage to an electromagnet having a given configuration of the magnetic circuit, and it is desired to produce by a winding any given number of ampere-turns of excitation, it is obvious that there are many ways of attaining the result with coils of various sizes and numbers of turns. If the resistance of the coil is so small relatively to the inductance as to be negligible, then there will only be one possible solution as to the number of turns. If, however, the resistance of the coil is of a magnitude comparable with that of its inductance, then there are various possible solutions, for an equal number of ampere-turns may be produced by using currents of different strengths and coils of different numbers of turns. In the cases of

different windings the lag of phase of the currents will be different. If the resistance is large relatively to the inductance, the difference of phase between the current and the impressed volts will be small, and the wasted watts large. If the inductance is large relatively to the resistance, the difference of phase will be nearly 90°; and the current will be nearly wattless, the efficiency being relatively high.

It is in accordance with good constructive practice to use such frequencies in the supply, and coils of such relatively high coefficients of self-induction as to justify the assumption, for the purpose of design, that the inductance is the important, and the resistance of the coil the unimportant matter. However, to bring the calculations to bear upon all cases that may occur, both resistance and inductance have been taken into consideration.

Let the impressed volts be called V, the current $i$ (both being square-root of mean square values), the resistance of the coil R, its coefficient of self-induction L, the frequency of the period of alternation $n$, and the number of windings W. The inductance will then be $2\pi n\mathrm{L}$, which for brevity may be written $p\mathrm{L}$. Then the impedance will be $\sqrt{\mathrm{R}^2+p^2\mathrm{L}^2}$. The relation between volts and amperes in the coil will be expressed as

$$\mathrm{V}=i\sqrt{\mathrm{R}^2+p^2\mathrm{L}^2}.$$

The angle of lag being called $\phi$, its sine will have the value

$$p\mathrm{L}\div\sqrt{\mathrm{R}^2+p^2\mathrm{L}^2}.$$

Hence we have the following relation :—

$$\mathrm{V}\,.\sin\phi=ip\mathrm{L}\,; \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

these being equivalent expressions for the effective part of the volts that is employed to balance the counter-electromotive force of self-induction in the coils. Now L is proportional to the square of the number of windings; and may be written $=k\mathrm{W}^2$, where $k$ is the coefficient of self-induction of a single turn, and W the number of windings.

Now, let the prescribed number of ampere-turns that are to be produced be called $\mathrm{Z}=i\mathrm{W}$. Inserting these values in (1) we obtain the expression

$$\mathrm{V}\sin\phi=kp\mathrm{WZ}\,; \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and finally

$$W = \frac{V \sin \phi}{kpZ}; \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

which is the relation sought.

4. The quantity $k$ denoted above, the coefficient of self-induction of a single turn, depends upon the dimensions of the iron parts of the magnetic circuit and upon those of the air-gap, as well as upon the permeability of the iron. If the magnetization is not carried beyond 5000 lines per square centimetre, the permeability may be considered as constant. But $k$ will decrease with any increase in the reluctance of the magnetic circuit, such as the lengthening of the air-gap. On the contrary, as the armature is attracted up toward the poles $k$ increases. The quantity $k$ represents the number of magnetic lines ($\times 10^{-9}$) which permeate the magnetic circuit when one ampere circulates in a single turn of wire around the core. We have only to multiply $k$ by the square of the number of windings to obtain the coefficient of self-induction of any coil subsequently to be wound upon this magnetic circuit. The quantity $k$ must itself be experimentally determined. This can be done by winding upon the magnetic circuit an experimental coil having a known number of turns $w$, and a known resistance $r$. Using this coil, measure the virtual current $c$ which passes when it is supplied at a voltage $v$ of frequency $n$. During the experiment the armature should be fixed, say by wooden distance-pieces, in the position which it will occupy in use. Then the coefficient of self-induction $l$ of the temporary coil will be

$$l = \sqrt{v^2 - c^2r^2} \div \sqrt{4\pi^2n^2c^2}.$$

Then $l$ being thus experimentally determined, it follows that $k = l/w^2$.

From the equation (3) we see that V, $p$, and $k$ being constant, there is a certain maximum number of windings which must not be exceeded if we are to get the prescribed number of ampere-turns of excitation; for $\sin \phi$ cannot be greater than unity. If this maximum number of windings is exceeded, the result will be to give fewer ampere-turns. This is easily seen if equation (3) be put into the form

$$Z=\frac{V\sin\phi}{kpW}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

Other things being equal, *the ampere-turns are inversely proportional to the number of windings.* This, at first sight, seems an anomaly; but is easily understood when we remember that the self-induction, and therefore the lessening of the current, is proportional to the square of the number of turns; so that whilst we are increasing our turns we are reducing our amperes in a much greater ratio.

Having ascertained $k$, the only other factor to be determined is $\sin\phi$. This in most practical cases can be assumed to be unity, since with the usual frequencies of supply and using magnets with iron cores, there is no difficulty in keeping the resistance negligibly small even when the number of windings is at the required maximum, so that $\phi$ is very nearly 90°. This will be seen from the results given below obtained from an actual magnet. In most ordinary cases, then, we merely write

$$W=V/kpZ\,; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

and, having calculated W, we find what current the wire will have to carry from the equation $i=ZW$. If there is room, and in most cases there will be ample, we may wind with thicker wire than is necessary to carry the current; but there is no advantage in using thicker wire than such as makes R practically negligible.

5. The following results are from actual experiment. The core and armature were those already described in relation to fig. 1. The iron core was wound with 140 turns of copper wire, 1·22 millim. in diameter, for the purpose of first determining $k$ when the armature was at the distances of 9·52, 6·35, 3·17, and 0 millim., respectively, from the poles. The resistance of the wire when heated by carrying 12 amperes was 0·3 ohm, and the frequency 93 periods per second. The fourth and fifth columns are worked out from the formulæ given above; for instance, in the first case

$$l=\frac{\sqrt{(31)^2-(12\times 0{\cdot}3)^2}}{2\pi\times 93\times 12}=0{\cdot}00434,$$

$$k=\frac{0{\cdot}00434}{(140)^2}=0{\cdot}221\times 10^{-6}.$$

| Air-gap (millimetres). | Virtual Volts at terminals of coil. | Virtual Amperes. | Coefficient of Self-induction $l$. | Self-induction of one turn. $k$. |
|---|---|---|---|---|
| 9·52 | 31 | 12 | 0·00434 | $0{\cdot}221 \times 10^{-6}$ |
| 6·35 | 35·6 | 12 | 0·005 | $0{\cdot}225 \times 10^{-6}$ |
| 3·17 | 46·8 | 12 | 0·00658 | $0{\cdot}336 \times 10^{-6}$ |
| 0 | 51 | 2·76 | 0·033 | $1{\cdot}68 \times 10^{-6}$ |

Suppose it were now required to wind the iron core so as to obtain 2400 ampere-turns when the armature was distant 9·52 millim. from the poles, using 50 volts and the same frequency as before.

Taking the equation (5) we obtain :

$$W = \frac{50}{0{\cdot}221 \times 10^{-6} \times 2 \times 3{\cdot}1416 \times 93 \times 2400} = 163 \text{ (approx.)}.$$

Accordingly 163 turns of wire 2·03 millimetres in diameter were wound upon the core. The current found, under the above conditions, to flow through the coil was 14·9 amperes, as measured by a Siemens' electrodynamometer. This shows that the coil produced 2430 ampere-turns, the error being well within what may be expected when using commercial measuring-instruments.

Some other results obtained with this magnet are given below (table, p. 141).

6. An advantage of the alternate-current electromagnet is the greater constancy in the pull which it exerts over a given range. If supplied at constant voltage a fairly constant pull on the armature can be obtained over a considerable range. The reaction set up by the core tends to set up a back-electromotive force the limiting value of which is equal to the impressed voltage. If the resistance of the coil were actually zero and the magnetic leakage also negligible, this limiting value would be attained. Now suppose that when acting upon its armature at a distance the self-inductive reaction chokes the current down to a certain value, the magnetization of the core going round cycles between definite maxima,

| | | | | |
|---|---|---|---|---|
| *Coil* 163 turns ; resistance (hot) 0·15 ohm. | | | | |
| Air-gap (millimetres). | Virtual Volts. | Virtual Amperes. | Coefficient of self-induction. | Self-induction of one turn. |
| 9·52 | 50 | 14·9 | 0·00574 | $0{\cdot}216 \times 10^{-6}$ |
| 6·35 | 50 | 12 | 0·00714 | $0{\cdot}268 \times 10^{-6}$ |
| *Coil* 274 turns ; resistance (hot) 0·6 ohm. | | | | |
| 9·52 | 50 | 5 | 0·01712 | $0{\cdot}228 \times 10^{-6}$ |
| 6·35 | 50 | 4·4 | 0·0194 | $0{\cdot}259 \times 10^{-6}$ |
| 3·17 | 50 | 3·5 | 0·0244 | $0{\cdot}326 \times 10^{-6}$ |

Suppose the core to be drawn in nearer to the pole, the reluctance of the magnetic circuit is lessened, and fewer ampere-turns will suffice to produce an equal magnetization; but because the reluctance is lessened the coefficient of self-induction is correspondingly increased, and the current choked in corresponding proportion. These two effects counterbalance one another, the magnetization going round cycles of practically the same amplitude as before. Hence the pull will be practically unchanged, save in so far as any change in the magnetic leakage at the different positions of the armature comes in to affect the question by weakening the field between the pole-faces and the armature. Were the pole-faces made relatively large so as to obviate the tendency to leakage and ensure the field being nearly uniform in the gap-spaces, the pull should be also very nearly constant throughout a range equal to at least one third of the breadth of the pole-face.

7. It is useful also to know the ratio between the different voltages that are needed, for a given electromagnet, to produce an equal number of ampere-turns with alternating and continuous electromotive forces.

Let $V_a$ stand for the alternating volts and $V_c$ for the continuous volts which must be applied to the terminals of the coil in order to produce equal virtual amperes. Then

$$\frac{V_a}{V_c} = \frac{\sqrt{R^2+p^2L^2}}{R}. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

When, as is generally the case, R is small compared with $pL$, we may take as a sufficient approximation

$$\frac{V_a}{V_c} = \frac{pL}{R}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

*The alternate voltage ratio is proportional to the frequency and to the time-constant of the electromagnet.*—For this ratio we may, on certain assumptions, find an expression in terms of the dimensions of the core and coil. Confining ourselves to the case where the magnetic circuit is closed, we may find the value of L as follows:—

Let $l_1$ be the length (in centimetres) of the iron magnetic circuit, $A_1$ its cross section, $v_1$ its volume, $m_1$ its mass in grammes, $\mu$ its permeability, and S the number of windings in the coil. Now $m_1 = 7{\cdot}79 v_1$. Then L (in henries) will be

$$L = 4\pi A_1 \mu S^2/10^9 l_1 = 4\pi v_1 \mu S^2/10^9 l_1^2 = 4\pi m_1 \mu S^2/7{\cdot}79 \times 10^9 l_1^2.$$

Assuming that B does not exceed 6000 lines per square centimetre, we may take for ordinary wrought-iron sheet $\mu = 2000$, and inserting this we obtain

$$L = S^2 m_1/310{,}000\, l_1^2.$$

Further, let $l_2$ be the mean length of one turn of the copper winding, $A_2$ the cross section of the copper wire, $k$ its conductivity (mhos per centimetre cube $= 10^6 \div 1{\cdot}63$), $v_2$ the volume of copper $(= SA_2 l_2)$, and $m_2$ the mass of copper $(= 8{\cdot}8 v_2)$. Then we have for the resistance of the coil

$$R = l_2 S/A_2 k = l_2^2 S_2^2/v_2 k = 8{\cdot}8 l_2^2 S_2^2/m_2 k.$$

Inserting these values for L and S we obtain:—

$$\frac{V_a}{V_c} = \frac{pL}{R} = \frac{2\pi n S^2 m_1}{310000 l_1^2} \times \frac{m_2 . 10^6}{8{\cdot}8 l_2^2 S^2}.$$

$$\frac{V_a}{V_c} = 1{\cdot}41 n \frac{m_1 m_2}{l_1^2 l_2^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

It is, however, doubtful, since the magnetic circuit contains two joints, whether so high a value as 2000 can be expected in ordinary work for $\mu$. In that case the coefficient 1·41 will be lower. With the electromagnet described above, at a frequency $n=93$, and with the armature in contact, the coefficient was 0·6 instead of 1·41. This is tantamount to saying that the working permeability was only 850. As so arranged, L being 0·044, the inductance $p$L was 25·26 ohms, and R was 0·15 ohm. The alternate voltage ratio was therefore about 170.

As the armature was removed from proximity to the poles the self-induction, and therefore the impedance, fell, making the voltage ratio for equal currents lower. When the armature was at 3·17 millim. the voltage ratio fell to 34, and at 9·52 millim. to 21·5.

It was stated above that in ordinary cases the ratio $p\mathrm{L}/\mathrm{R}$ might be taken instead of the more complete expression of equation (6). If it is desired to obtain a nearer approximation to $\sqrt{\mathrm{R}^2+p^2\mathrm{L}^2}/\mathrm{R}$ than is afforded by simply neglecting the R under the square-root sign, we may take the value

$$\frac{\mathrm{V}_a}{\mathrm{V}_c}=\frac{p\mathrm{L}}{\mathrm{R}}+\frac{\mathrm{R}}{2p\mathrm{L}},$$

which, by reference to the preceding numerical instances, shows that the correcting term is really negligible, being in the first case, where $p\mathrm{L}/\mathrm{R}$ was 170, only $\frac{1}{340}$, and in the last case, where $p\mathrm{L}/\mathrm{R}$ was 21·5, only $\frac{1}{43}$, less than $\frac{1}{8}$ of 1 per cent.

8. Lastly, a very simple expression can be found for the number of windings, in terms of any desired mean value of the magnetic flux **N** in the iron. For if the iron of cross-section A is subjected to cycles of magnetization in which the mean value of the permeation is **B**, the mean flux is $\mathbf{N}=\mathrm{A}\mathbf{B}$, and if the frequency be $n$ periods per second, the self-induced electromotive force in W windings surrounding the iron will be equal to $2\pi n\mathrm{W}\mathbf{N}\div 10^8$ volts. If, then, the resistance is negligibly small, this may be equated to V, the mean volts of supply, whence we obtain at once

$$\mathrm{W}=\frac{\mathrm{V}\times 10^8}{p\mathbf{N}}. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (9)$$

For example :—Suppose that in the above magnet it were desired to obtain a permeation of 4000 lines to the square centimetre, the total number of lines **N** would equal the area A (6·5 square centim.) multiplied by 4000, or $\mathbf{N}=26{,}000$. Taking the volts as 50, and the periods per second as 93, we find by formula (9), $W=329$.

## DISCUSSION.

Prof. PERRY pointed out that the constant pull of the alternate-current magnet followed immediately from the fundamental equation $e=rc+n\dot{I}$, where $rc$ is small, for if $e$ be constant then $\dot{I}$ and therefore I and $I^2$ are constant. He was interested to see that the pulls for equal ampere-turns were the same, and indicated how the problem could be worked out mathematically when hysteresis was taken into account.

Mr. BLAKESLEY thought it better to fill the space on a magnet full of copper rather than use wire only just large enough to carry the current, for the loss of energy would be reduced. Some of the formulæ given might be put in simpler form.

Mr. SWINBURNE said an alternate-current magnet would only give constant pull in special cases. As another rule for winding alternate-current magnets, he said, wind the magnets as for continuous currents, and put a condenser in to take the same current, thereby reducing the voltage required.

Mr. BLAKESLEY said it would require a capacity of 600 microfarads to suit the magnet mentioned in the paper.

Dr. THOMPSON, in reply, agreed with Mr. Blakesley that the condenser was impracticable in many cases.

# XV. *On Electromagnetic Induction in Plane, Cylindrical, and Spherical Current-Sheets, and its Representation by Moving Trails of Images.* *By* G. H. BRYAN, *M.A.*[*]

## PART I.—GENERAL EQUATIONS—PLANE SHEETS.

### *Introduction.*

1. IT is well known that if a very thin, indefinitely extended plane sheet of metal of finite conductivity is placed in a varying magnetic field due to the presence of moving magnetic poles in its neighbourhood, induction-currents are set up in the sheet and the field of force due to these currents may be represented by a moving trail of images.

In the present paper the surface-conditions which hold at the surface of a plane, cylindrical, spherical, or other conducting sheet of uniform small thickness are deduced directly from the fundamental laws of electromagnetic induction. By working directly with the scalar magnetic potential, and avoiding the introduction of the vector potential and the quantity which Maxwell denotes by P, the investigations are much simplified. Moreover, in at least one comparatively recently published paper the boundary conditions satisfied by the vector potential at the surface of separation of two different media have been erroneously stated, and for this reason it is advantageous to employ a method which obviates the difficulty.

The results will be employed to show how the field due to the presence of a magnetic pole of varying intensity in the neighbourhood of a plane, cylindrical, or spherical current-sheet may be represented by means of a moving trail of images. By the principle of superposition the effect of any number of poles of varying intensity can be deduced, and the corresponding expressions for the field can thus be obtained when the variable inducing system of magnets is of the most general possible character, as, for example, one (or more) magnetic poles moving about in any manner whatever.

In this way a synthetic solution of the problem of induction in current sheets is obtained. The phenomena of induction in spherical and other current sheets have been treated at considerable length from an analytical point of view by Larmor, Lamb, and Niven, and the last-named writer has made some attempt, in the case of a sphere, to interpret the results by means of images; but the present investigation seemed desirable for many reasons, and it is hoped that it will overcome some of the difficulties, and elucidate some of the obscurities which present themselves in most treatments of this interesting application of the principles of electromagnetism.

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[*] Read May 11, 1894.

### *Fundamental Assumptions.*

2. The laws of electromagnetic induction assert that in bodies at rest

I. *The total current across any enclosed portion of a surface which always contains the same particles is equal to* $1/4\pi$ *of the line-integral of magnetic force round the curve bounding the surface.*

II. *The rate of decrease of the surface-integral of magnetic induction across any enclosed surface which always contains the same particles is equal to the line-integral of electromotive force round the curve bounding the surface.*

In applying these laws to an infinite dielectric separated into two portions by a thin conducting sheet, it is usually assumed that the disturbance produced by the inducing system is not a very rapidly alternating one, so that displacement currents in the dielectric have no appreciable magnetic effect*. With this assumption, the magnetic force in the dielectric will always be derivable from a potential which will only depend on the inducing system and the currents in the sheet. In other words, the state of the dielectric will be given by an "equilibrium theory."

It is also assumed that the induction-currents at any point distribute themselves uniformly throughout the thickness of the sheet. This requires that the disturbance shall not be a very rapidly alternating one, and also that the thickness of the sheet shall be very small compared with the other linear dimensions of the system (such as the distances of the moving poles, the radius of the sheet if spherical, &c.).

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* Watson and Burbury, 'Mathematical Theory of Electricity and Magnetism,' ii. § 405.

### *Surface Conditions at a Plane-Current Sheet.*

3. Let the plane of the sheet be taken as the plane of $x$, $y$, let the thickness of the sheet be $c$, and specific conductivity C.

Let $\Omega_1$, $\Omega_2$ be the magnetic potentials on the negative and positive side of the sheet respectively, $\phi$ the current function in the sheet at any point. Apply Law I. to the circuit formed by going along the positive side of the sheet from the origin to any point and returning along the negative side from that point to the origin. Since the thickness of the sheet is small, the terms contributed to the line-integral of the magnetic force by the passage of the circuit from one side of the sheet to the other may be neglected and we obtain *

$$\Omega_2-\Omega_1=4\pi\phi+\text{constant}. \quad . \quad . \quad . \quad . \quad (1)$$

Now apply Law II. to any circuit $s$ drawn in the plane of the sheet. Let $S_1$, $S_2$ be two surfaces drawn in the dielectric infinitely near to the positive and negative faces of the sheet respectively and both bounded by the curve $s$, and let P, Q be the components of electromotive force at any point. Then, assuming the magnetic permeability of the dielectric to be unity, we have

$$\int(\mathrm{P}dx+\mathrm{Q}dy)\text{ round }s=\frac{d}{dt}\iint\frac{d\Omega_1}{dz}\,d\mathrm{S}_1=\frac{d}{dt}\iint\frac{d\Omega_2}{dz}\,d\mathrm{S}_2,$$

and since corresponding elements of the near surfaces $S_1$, $S_2$ are equal, it is evident that

$$\frac{d\Omega_1}{dz}=\frac{d\Omega_2}{dz} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

at the surface, so that the normal component of magnetic induction is continuous, as it should be †.

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[*] Maxwell, 'Electricity and Magnetism,' ii. § 653.

[†] The magnetic permeability of the sheet itself will not affect the conditions of the problem unless it is required to proceed to a higher order of approximation by taking into account first powers of the thickness (or unless the sheet is formed of soft iron whose magnetic permeability may be large).

Again, the equations of conduction give

$$CcP=\frac{d\phi}{dy},\quad CcQ=-\frac{d\phi}{dx}.$$

Hence

$$\frac{d}{dt}\iint\frac{d\Omega_1}{dz}dS=\frac{d}{dt}\iint\frac{d\Omega_2}{dz}dS=\frac{1}{Cc}\int\left(\frac{d\phi}{dy}\frac{dx}{ds}-\frac{d\phi}{dx}\frac{dy}{ds}\right)ds$$

$$=-\frac{1}{Cc}\int\left(\frac{d\phi}{dy}\frac{dy}{dn}+\frac{d\phi}{dx}\frac{dx}{dn}\right)ds=-\frac{1}{Cc}\int\frac{d\phi}{dn}ds$$

$$=-\frac{1}{Cc}\iint\left(\frac{d^2\phi}{dx^2}+\frac{d^2\phi}{dy^2}\right)dS,$$

where $dn$ is the element of the outward-drawn normal to $s$ and the surface-integral taken over the area S of the sheet bounded by the curve $s$.

Hence at the surface of the sheet

$$\frac{d}{dt}\frac{d\Omega_1}{dz}=\frac{d}{dt}\frac{d\Omega_2}{dz}$$

$$=-\frac{1}{Cc}\left(\frac{d^2\phi}{dx^2}+\frac{d^2\phi}{dy^2}\right)$$

$$=-\frac{1}{4\pi Cc}\left(\frac{d^2}{dx^2}+\frac{d^2}{dy^2}\right)(\Omega_2-\Omega_1)\qquad\text{by (1)}$$

$$=\frac{1}{4\pi Cc}\frac{d^2}{dz^2}(\Omega_2-\Omega_1)\quad .\ .\ .\ .\ .\quad (3)$$

(remembering that $\nabla^2\Omega_1=0$ and $\nabla^2\Omega_2=0$).

4. Now let $\Omega_0$ be the magnetic potential due to the external or inducing system, $\Omega'$ and $\Omega''$ the magnetic potentials on the two sides due to the sheet itself, so that

$$\Omega_1=\Omega_0+\Omega',\quad \Omega_2=\Omega_0+\Omega''.\quad .\ .\ .\ .\quad (4)$$

Then $\Omega_0$ and its differential coefficients with respect to $z$ are continuous in crossing the sheet, while from the symmetry of the field due to the sheet

$$\Omega'(x,y,z)=-\Omega''(x,y,-z),\quad .\ .\quad (5)$$

so that

$$\frac{d^n\Omega'}{dz^n}=(-1)^{n+1}\frac{d^n\Omega''}{dz^n}.$$

Therefore the surface condition (3) gives

$$\frac{d}{dt}\frac{d\Omega'}{dz}+\frac{d}{dt}\frac{d\Omega_0}{dz}=-\frac{1}{2\pi Cc}\frac{d^2\Omega'}{dz^2}, \quad . \quad . \quad . \quad (6)$$

$$\frac{d}{dt}\frac{d\Omega''}{dz}+\frac{d}{dt}\frac{d\Omega_0}{dz}=+\frac{1}{2\pi Cc}\frac{d^2\Omega''}{dz^2} \quad . \quad . \quad . \quad (7)$$

as the surface conditions satisfied by the potential at the two sides of the sheet.

### *Surface Conditions at a Cylindrical Sheet.*

5. Using cylindrical coordinates, let $r=a$ be the equation of the middle surface of a cylindrical current-sheet, and let its thickness $c$ be so small that the corresponding elements of its bounding surfaces and middle surface, viz.

$$(a-\tfrac{1}{2}c)\,d\theta dz,\ (a+\tfrac{1}{2}c)\,d\theta\,dz, \text{ and } a\,d\theta dz,$$

are to be regarded as equal.

If $\Omega_1$, $\Omega_2$ are the magnetic potentials inside and outside the sheet, we shall still have as for a plane sheet

$$\Omega_2-\Omega_1=4\pi\phi+\text{constant}; \quad . \quad . \quad . \quad . \quad (1)$$

and by application of the second law to the small circuit bounding the surface-element $a\,d\theta dz$, we have at the sheet

$$\frac{d}{dt}\frac{d\Omega_1}{dr}=\frac{d}{dt}\frac{d\Omega_2}{dr}=-\frac{1}{Cc}\left\{\frac{d}{rd\theta}\frac{d\phi}{rd\theta}+\frac{d^2\phi}{dz^2}\right\}$$

$$=-\frac{1}{4\pi Cc}\left\{\frac{1}{r^2}\frac{d^2}{d\theta^2}+\frac{d^2}{dz^2}\right\}(\Omega_2-\Omega_1)$$

$$=\frac{1}{4\pi Cc}\left(\frac{d^2}{dr^2}+\frac{1}{r}\frac{d}{dr}\right)(\Omega_2-\Omega_1),$$

or

$$\frac{d}{dt}\left(r\frac{d\Omega_1}{dr}\right)=\frac{d}{dt}\left(r\frac{d\Omega_2}{dr}\right)=\frac{1}{4\pi Cc}\frac{d}{dr}r\frac{d}{dr}(\Omega_2-\Omega_1). \quad . \quad . \quad (8)$$

### *Surface Conditions at a Spherical Sheet.*

6. In the case of a spherical sheet of small thickness, we obtain in like manner

$$\frac{d}{dt}\frac{d\Omega_1}{dr}=\frac{d}{dt}\frac{d\Omega_2}{dr}=\frac{1}{4\pi Cc}\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}\right)(\Omega_2-\Omega_1),$$

or

$$\frac{d}{dt}\left(r^2\frac{d\Omega_1}{dr}\right)=\frac{d}{dt}\left(r^2\frac{d\Omega_2}{dr}\right)=\frac{1}{4\pi Cc}\frac{d}{dr}r^2\frac{d}{dr}(\Omega_2-\Omega_1). \quad (9)$$

### *Extension to Curved Sheets of other Forms.*

7. When the sheet is of any form other than those above considered, it is necessary to assume a certain law of variation of the thickness in order to put the boundary conditions into a form similar to those given above *.

Let us use orthogonal coordinates $\alpha$, $\beta$, $\gamma$; let the line-element be given by

$$ds^2 = \frac{d\alpha^2}{h_1^2} + \frac{d\beta^2}{h_2^2} + \frac{d\gamma^2}{h_3^2},$$

and let the equation of the current sheet be

$$\gamma = \text{constant}.$$

Equation (1) still holds, and by applying Law II. to the circuit enclosed on the sheet by the curves $\alpha$, $\alpha + \delta\alpha$, $\beta$ and $\beta + \delta\beta$, we have the surface-condition

$$\frac{1}{h_1 h_2} \frac{d}{dt} h_3 \frac{d\Omega_1}{d\gamma} = \frac{1}{h_1 h_2} \frac{d}{dt} h_3 \frac{d\Omega_2}{d\gamma}$$

$$= -\frac{d}{d\alpha}\left\{\frac{h_1}{Cch_2}\frac{d\phi}{d\alpha}\right\} - \frac{d}{d\beta}\left\{\frac{h_2}{Cch_1}\frac{d\phi}{d\beta}\right\}$$

$$= -\frac{1}{4\pi}\left\{\frac{d}{d\alpha}\left(\frac{h_1}{Cch_2}\frac{d}{d\alpha}\right) + \frac{d}{d\beta}\left(\frac{h_2}{Cch_1}\frac{d}{d\beta}\right)\right\}(\Omega_2 - \Omega_1). \quad (10)$$

But Laplace's equation which is satisfied by $\Omega_1$ $\Omega_2$ may be written

$$\frac{d}{d\alpha}\left(\frac{h_1}{h_2 h_3}\frac{d\Omega}{d\alpha}\right) + \frac{d}{d\beta}\left(\frac{h_2}{h_3 h_1}\frac{d\Omega}{d\beta}\right) + \frac{d}{d\gamma}\left(\frac{h_3}{h_1 h_2}\frac{d\Omega}{d\gamma}\right) = 0.$$

Hence it is possible to eliminate differential coefficients with respect to $\alpha$, $\beta$ from the surface-condition if, and only if,

$$Cc \propto h_3. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Hence the thickness of the sheet at any point must be inversely proportional to the distance between two neighbouring surfaces of the family $\gamma = \text{constant}$ at that point. In the case of an ellipsoidal sheet this leads to the well-known condition that the thickness must be proportional to the perpendicular on the tangent-plane, or that the sheet must be a shell bounded by similar and similarly situated ellipsoids.

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* Compare Watson and Burbury, §426.

Writing

$$R=\frac{h_3}{2\pi Cc}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

the surface-condition now becomes

$$\frac{d}{dt}\left(\frac{h_3}{h_1h_2}\frac{d\Omega_1}{d\gamma}\right)=\frac{d}{dt}\left(\frac{h_3}{h_1h_2}\frac{d\Omega_2}{d\gamma}\right)=\frac{R}{2}\frac{d}{d\gamma}\left\{\frac{h_3}{h_1h_2}\frac{d}{d\gamma}(\Omega_2-\Omega_1)\right\} \quad (13)$$

*Synthetic Determination of the Images in a Plane Sheet.*

8. In order to illustrate the synthetic method, consider its application to the well-known case of a plane-current sheet. Let the induced currents be excited by a magnetic pole placed at the fixed point $(x_0, y_0, z_0)$ on the positive side of the sheet whose strength is $f(t)$ an arbitrary function of the time. Then

$$\Omega_0=\frac{f(t)}{\{(x-x_0)^2+(y-y_0)^2+(z-z_0)^2)\}^{\frac{1}{2}}}, \quad . \quad . \qquad (14)$$

and the surface-condition satisfied by $\Omega'$ the potential on the negative side is

$$\frac{d^2\Omega'}{dzdt}+R\frac{d^2\Omega}{dz^2}=-\frac{d^2\Omega_0}{dzdt}, \quad . \quad . \quad . \quad . \qquad (15)$$

where

$$R=\frac{1}{2\pi Cc}. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (16)$$

Integrating (15), the value obtained for $\Omega'$ is found to be the potential due to magnetic poles or images on the positive side of the sheet, and these are outside the region over which the solution is required to hold, as they should be. We have

$$\left(\frac{d}{dt}+R\frac{d}{dz}\right)\Omega'=-\frac{f'(t)}{\sqrt{\{(x-x_0)^2+(y-y_0)^2+(z-z_0)^2\}}},$$

$$\therefore \quad \Omega'=-\int_{-\infty}^{t} e^{-R(t-\tau)\frac{d}{dz}}\frac{f'(\tau)}{\sqrt{\{(x-x_0)^2+(y-y_0)^2+(z-z_0)^2\}}}d\tau$$

$$=-\int_{-\infty}^{t}\frac{f'(\tau)}{\sqrt{\{(x-x_0)^2+(y-y_0)^2+(z-z_0-Rt+R\tau)^2\}}}d\tau$$

$$=-\frac{f(t)}{\sqrt{\{(x-x_0)^2+(y-y_0)^2+(z-z_0)^2\}}}$$

$$+\int_{-\infty}^{t}Rf(\tau)\frac{d}{dz}\frac{1}{\sqrt{\{(x-x_0)^2+(y-y_0)^2+(z-z_0-Rt+R\tau)^2\}}}d\tau. \quad (17)$$

The first term represents the effect of a pole equal and opposite to the given pole at the point $(x_0, y_0, z_0)$, while the second term shows that the effect of the action of the pole between the times $\tau$ and $\tau+\delta\tau$ is represented at time $t$ by a magnet of strength $\mathrm{R}f(\tau)\delta\tau$ situated at the point $(x_0, y_0, z_0+\mathrm{R}(t-\tau))$. The potential at the positive side is found from the relation (5), or

$$\Omega''(x,y,z)=-\Omega'(x,y,-z).$$

When the pole is in motion the results thus arrived at enable us to plot out the moving images contributed during every time element $\delta\tau$ of the motion in the well-known way, or they may be obtained as follows:—

9. If, instead of a single magnetic pole, we are dealing with a magnetic distribution on the positive side of the sheet such that the volume-density of magnetism of the point $(x_0\, y_0\, z_0)$ is $\mathrm{F}(x_0\, y_0\, z_0\, t)$, we must write $\mathrm{F}(x_0\, y_0\, z_0\, t)\, dx_0\, dy_0\, dz_0$ for $f(t)$ in the expressions for $\Omega_0$ and $\Omega'$. Hence we have

$$\Omega_0=\int_0^\infty\int_{-\infty}^\infty\int_{-\infty}^\infty \frac{\mathrm{F}(x_0\, y_0\, z_0\, t)\, dx_0\, dy_0\, dz_0}{\{(x-x_0)^2+(y-y_0)^2+(z-z_0)^2\}^{\frac{1}{2}}}, \quad . \quad . \quad . \quad (18)$$

$$\Omega'=-\Omega_0-\int_{-\infty}^t d\tau\int_0^\infty dz_0\int_{-\infty}^\infty\int_{-\infty}^\infty \mathrm{RF}(x_0\, y_0\, z_0\, \tau)$$
$$\frac{z-z_0-\mathrm{R}(t-\tau)}{\{(x-x_0)^2+(y-y_0)^2+(z-z_0-\mathrm{R}(t-\tau))^2\}^{\frac{3}{2}}}\, dx_0\, dy_0. \quad (19)$$

If now the inducing system consists of a single pole of strength $f(t)$ which moves about *in any manner* so that its coordinates at any time $t$ are $\xi(t)$, $\eta(t)$, $\zeta(t)$, functions of $t$, we have

$$\mathrm{F}(x_0\, y_0\, z_0\, \tau)=0,$$

except when $x_0=\xi(\tau)$, $y_0=\eta(\tau)$, $z_0=\zeta(\tau)$, and then

$$\mathrm{F}(x_0\, y_0\, z_0\, \tau)\, dx_0\, dy_0\, dz_0=f(\tau).$$

Therefore

$$\Omega_0=\frac{f(t)}{\{(x-\xi(t))^2+(y-\eta(t))^2+(z-\zeta(t))^2\}^{\frac{1}{2}}}, \quad . \quad . \quad . \quad . \quad (20)$$

$$\Omega'=-\Omega_0$$
$$-\int_{-\infty}^t \mathrm{R}f(\tau)\frac{z-\zeta(\tau)-\mathrm{R}(t-\tau)}{\{(x-\xi(\tau))^2+(y-\eta(\tau))^2+(z-\zeta(\tau)-\mathrm{R}(t-\tau))^2\}^{\frac{3}{2}}}\, d\tau. \quad (21)$$

This is the expression for the magnetic potential due to the induced currents on the negative side of the sheet, *i. e.* on the opposite side to the moving pole; and it is to be observed that $z$ is taken to be negative on this side.

The quantity $\Omega''$, which represents the potential due to the induced currents on the positive side (where $z$ is positive), is given by

$$\Omega''=\frac{f(t)}{\{(x-\xi(t))^2+(y-\eta(t))^2+(z+\zeta(t))^2\}^{\frac{1}{2}}}$$

$$-\int_{-\infty}^{t}\mathrm{R}f(\tau)\,\frac{z+\zeta(\tau)+\mathrm{R}(t-\tau)}{\{(x-\xi(\tau))^2+(y-\eta(\tau))^2+(z+\zeta(\tau)+\mathrm{R}(t-\tau))^2\}^{\frac{3}{2}}}\,d\tau \quad (22)$$

and the complete expression for the potential due to the induced currents and the moving pole itself is, by (4),

$$\Omega_2=\Omega_0+\Omega''.$$

10. The components of magnetic force at $(x, y, z)$ due to the induced currents alone are respectively

$$-\frac{d\Omega''}{dx},\quad -\frac{d\Omega''}{dy},\quad -\frac{d\Omega''}{dz};$$

and the components of the force on the pole itself at any time $t$ are found by multiplying these expressions by the strength of the pole, *i. e.* by $f(t)$, and putting $x=\xi(t)$, $y=\eta(t)$, $z=\zeta(t)$ *after* the differentiations have been performed.

In particular, if the pole moves along a straight line perpendicular to the plate, and we take this line as axis of $z$, the force on the moving pole itself

$$=f(t)\times\left\{\frac{f(t)}{\{2\zeta(t)\}^2}-2\,\mathrm{R}\int_{-\infty}^{t}\frac{f(\tau)\,d\tau}{\{\zeta(t)+\zeta(\tau)+\mathrm{R}(t-\tau)\}^3}\right\}. \quad (23)$$

The well-known case in which a pole is suddenly generated at the time $t=0$, and its strength remains constant and equal to $m$ after that time, is deduced by making

$$f(t)=0 \text{ from } t=-\infty \text{ to } t=0,$$

$$f(t)=m \text{ from } t=0 \text{ to } t=+\infty.$$

We therefore have to write $m$ for $f(t)$ in the above expressions and to reduce the inferior limit of integration with respect to $\tau$ from $-\infty$ to 0.

The advantage of starting with a fixed instead of a moving pole is more evident in the case of a cylindrical or spherical sheet, especially in the latter, since we are thus enabled to use zonal spherical harmonics only and the analysis is consequently much simplified.

## Discussion.

Prof. Minchin showed that equation (1) of the paper ($\Omega_2 - \Omega_1 = 4\pi\phi +$ constant, where $\Omega_2$ and $\Omega_1$ are the magnetic potentials at the two sides of the sheet, and $\phi$ the current function) could be deduced by purely mathematical reasoning, instead of being based on the laws of electromagnetic induction. Moreover it was true of any function whatever, and did not depend on $\phi$ being the current function. Equation (2),

$$\left(\frac{d\Omega_2}{dz} = \frac{d\Omega_1}{dz}\right),$$

followed immediately from the fact that the magnetic force was continuous. The latter part of the paper might be simplified by integrating the linear partial differential equation (15)

$$\left(\frac{d^2\Omega_1}{dz\,dt} - \mathrm{R}\frac{d^2\Omega_1}{dz^2} = -\frac{d_2\Omega_0}{dz\,dt}\right)$$

in the ordinary way, for the form was one for which the auxiliary equations are well known.

Dr. Burton, in reply, said he thought Mr. Bryan's reason for developing the equations from the laws of electromagnetic induction was to give his work a physical rather than a mathematical basis.

## XVI. *On Dielectrics.* *By* ROLLO APPLEYARD [*].

MOST dielectrics, when submitted to the ordinary "insulation" test, show an apparent increase of resistance under the action of the testing-current. That is to say: from the moment the current has been applied, the galvanometer-spot, having reached its maximum position, falls gradually towards zero with time. The rate of this diminution, at any instant, is a measure of the so-called "electrification" of the dielectric at that instant. For commercial purposes the "electrification" is usually computed between the first and second minutes from the moment of charge; the value thus determined is an excellent confirmatory guide to quality, if the general history of the material and the peculiarities of manufacture are understood. But, apart from its merely commercial bearing, "electrification" presents a wide field for scientific research. The use of the term "electrification" for this rate of change of the apparent resistance of a dielectric with the time of application of the charging current, may be called into question by those who prefer the words "polarization," or "absorption;" but, in the present stage of our knowledge of the action which determines this change, it has been thought better to adopt a term which is never mistaken in practice than to use an ambiguous expression, founded upon an equally uncertain hypothesis. "Electrification" seems to be the net result of many simultaneous actions, some of which are very obscure; the physical mechanism implied in the process is subtle and mysterious, the experimental observations are difficult to reconcile among themselves, and there is no theory to adequately account for the phenomena. It is not proposed, here, to make any attempt at solving the difficulties, but rather to present them in the form of experimental results.

### *Celluloid.*

The first substance to be dealt with, in this regard, is "celluloid." As far as can be judged by inspection it appears to be a compound of guncotton and camphor, with a trace of lime—possibly in the form of sulphate. When seen through the microscope, small white spots become visible in a translucent yellowish substance. In texture "celluloid" resembles "cordite," but it is of lighter colour, inflammable but not explosive. The insulation of this substance was, at first, measured in the following way:—A thin circular sheet of celluloid was placed between two plane surfaces of brass 11 inches in diameter. A margin of celluloid was allowed, to prevent leakage over the edges; and a heavy weight was put upon the top plate. When this sheet was submitted to the action of a current, there was no such apparent increase of resistance as is usually to be observed with dielectrics. The galvanometer, in fact, indicated the reverse effect—the deflexion gradually increasing with time. No actual fault could be detected in any of the samples, and yet the "electrification" was negative. This curious effect was the more to be noticed as the voltage of the testing-battery was increased. The actual insulation resistance, calculated for the same sample, with this apparatus, under various currents, showed that the resistance changed enormously with the testing voltage.

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[*] Read May 11, 1894.

In this case, and in all experiments here mentioned, the insulation has been computed from the deflexions obtained after the corresponding voltage had been applied for one minute. The upper readings correspond with increasing voltages; the lower curve completes the cycle with diminishing voltages, and shows the falling-off of insulation with current, in a manner curiously like the hysteresis curve of iron. The observed values are given in Table I.

TABLE I.—Celluloid Sheet.

| | | volts 150 | volts 300 | volts 600 | volts 750 | volts 600 | volts 300 | volts 150 |
|---|---|---|---|---|---|---|---|---|
| Galvanometer Readings. | $1^{m}$... | 19·8 | 85·8 | 533 | 1310 | 605 | 152 | 45 |
| | $2^{m}$... | 20 | 89·3 | 554 | 1338 | 663 | 158 | 45 |
| Corresponding Resistance in megohms. | = | 4040 | 1840 | 597 | 303 | 526 | 1039 | 1778 |

This table includes the actual galvanometer-deflexions from which the insulation-resistance at each voltage was calculated. First and second minute readings are recorded, and exhibit very strikingly the apparently *negative* "electrification,"—the first-minute readings being less than the second-minute readings.

A series of tests was made upon celluloid sheets pressed, in the above manner, between two plane surfaces of metal, and the same general features were observed in each case. As no definite fault could be discovered in any sample, I was led to suppose that the abnormal change in resistance, and the corresponding negative "electrification," were to be accounted for by some complex molecular rearrangement within the substance of the celluloid itself. Leakage over the edges might obviously be urged in explanation, but the conditions did not seem to allow of any serious loss in this manner. While employing unyielding metallic surfaces against the comparatively hard surface of the celluloid, the chances of uneven pressure upon the sheet were very great: which would imply uneven electrical contact between the dielectric and the plates.

The next experiments were made with a view to test the celluloid in perfect contact with the opposed plates; to remove all chances of leakage-error; and to provide, at the same time, a more evenly distributed pressure over the surface. The hard metallic plates were therefore replaced by mercury surfaces which conformed precisely, and without undue pressure, to the sheet of dielectric; and, at the same time, made perfect contact with it, leaving no air-spaces or spark-gaps where ozone or other gases might collect.

Circular sheets of celluloid, 11½ inches in diameter, were employed for these tests. To prevent leakage, a 3-inch margin was allowed all round, so that the working-surface in contact with mercury was 5½ inches in diameter. The method of fixing the dielectric sheet was as follows:—Two flat ebonite rings, 5½ inches internal diameter, and 6½ inches outside, were faced on each side with india-rubber, forming insulating washers. These rings were placed exactly opposite each other, flatwise, one on each side of the sheet to be tested. Circular plates of iron were now laid against the outer faces of the rings, and combined to make two mercury-tight hollow boxes, one on each side of the dielectric. The whole was then gripped vertically in an ebonite vice; after which mercury was poured in to fill the boxes. This apparatus, with the exception of the insulating rings, is the same as that designed, I believe, by Mr. Evers. The great advantage of the method is that the mercury conforms to the surface of the dielectric, leaving no air-spaces and necessitating no artificial pressure. The surface-leakage can be made as small as desired, by the simple device of leaving enough margin. Experiments made upon dielectrics fixed in this apparatus give results entirely different from those obtained with rigid metallic plates.

A sheet of celluloid ·071 inch in thickness was the first that came under trial. Its behaviour during a cycle of voltage from 150 to 1200 volts is represented in Table II.

Table II.

| Volts *increasing.* | | Volts *diminishing.* | |
|---|---|---|---|
| Volts. | Resistance in megohms. | Volts. | Resistance in megohms. |
| 150 | 82·7 | 1050 | 80·7 |
| 300 | 82·3 | 900 | 81·0 |
| 450 | 82·0 | 750 | 81·3 |
| 600 | 81·5 | 600 | 81·5 |
| 750 | 81·2 | 450 | 82·0 |
| 900 | 80·8 | 300 | 82·3 |
| 1050 | 80·6 | 150 | 82·7 |
| 1200 | 80·6 | | |

The curves practically overlap. The insulation falls somewhat with the increase of voltage, but recovers its original value as the cycle is completed. There was no observable "electrification"; the first and second minute readings were in each case identical.

The next sheet of celluloid tested was 6 mils in thickness. Here again there was no sign of "electrification," though there was a distinct diminution of insulation with voltage.

This sheet broke down at 1200 volts; there is nothing in the curve to indicate that such a rupture was about to take place. These results are given in Table III.

TABLE III.

| Volts *increasing.* | Resistance in megohms. |
|---|---|
| 150 | 30·0 |
| 300 | 29·6 |
| 450 | 29·2 |
| 600 | 28·4 |
| 750 | 27·7 |
| 900 | 26·8 |
| 1050 | 26·0 |
| 1200 | Broke down. |

A third sheet, cut from the same specimen as the last, was then tested through a cycle from 150 to 1050 volts; it showed practically no hysteresis and no "electrification," the return values being simply reproductions of the rising ones. There is the same drop in insulation with voltage as in the previous tests, as shown by Table IV.

TABLE IV.

| Volts *increasing.* | | Volts *diminishing.* | |
|---|---|---|---|
| Volts. | Resistance in megohms. | Volts. | Resistance in megohms. |
| 150 | 26·34 | 900 | 22·72 |
| 300 | 25·56 | 750 | 23·48 |
| 450 | 24·93 | 600 | 24·15 |
| 600 | 24·15 | 450 | 24·93 |
| 750 | 23·51 | 300 | 25·68 |
| 900 | 22·72 | 150 | 26·52 |
| 1050 | 21·89 | | |

The same sheet was then tested between hard metallic plates, the results are indicated in Table IV. A.

TABLE IV. A.

| | volts 150 | volts 300 | volts 450 | volts 600 | volts 750 | volts 900 | volts 1050 | volts 900 | volts 750 | volts 600 | volts 450 | volts 300 | volts 150 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1m | 6 | 23·5 | 61·5 | 161 | 278 | 156 | 158 | 186 | 127 | 117·0 | 95·0 | 39·5 | 11·5 |
| 2m | ...... | 23·7 | 64·0 | 171 | 296 | 162 | 162 | 189 | 129 | 118·5 | 96·5 | 39·5 | ...... |
| | megohms<br>20,550 | 10440 | 6047 | 3076 | 870 | 283 | 135 | 199 | 549 | 1641 | 3915 | 6212 | 10720 |

## *"Dielectric Hysteresis."*

"Dielectric hysteresis" is here alluded to in a sense which needs a little explanation. The similarity in shape and character between some of these curves and the well-known forms of the hysteresis curves of magnetism is all that I wish to imply,—it is *not* the phenomenon of "dielectric hysteresis" proper. In an article in the *Electrotechnische Zeitschrift*, 29th April, 1892, p. 227, Steinmetz traces the analogy between a dielectric medium in an electrostatic field and magnetic bodies in a magnetic field, with a view to determining whether the loss of energy in dielectrics, under the influence of an alternating electrostatic field, would follow a law similar to that which defines the magnetic losses due to magnetic hysteresis. The experiments of Steinmetz, and of Arno, have gone to show that the energy expended in a dielectric medium, in an electrostatic field of alternating potential, is sensibly proportional to the square-root of the intensity of the electrostatic field. These losses are due to "dielectric hysteresis" proper, and are quite distinct from the mere change of resistance with voltage here described. The experimental results of Steinmetz should, however, be corrected for this other phenomenon of change, which, for the time being, we may call "dielectric mutability," or any other term which denotes the variation of resistance with voltage; for it is clear that the energy expended during a cycle of potential cannot rightly be calculated upon the basis of constant resistance assumed by Steinmetz. With this correction, if it could be determined and applied to his results, the observed values, notwithstanding their present close agreement with those calculated, may possibly be brought even nearer to conformity.

### *"Residual Charge."*

The residual charge becomes a very small quantity a few minutes after breaking circuit; consecutive voltages can therefore be applied without having to wait very long for the practical disappearance of the last charge. In the above tests it was made a rule never to send a current into a sheet until the previous charge had vanished to within ½ per cent. Although, under these conditions, the charge is quickly got rid of, yet during the first few seconds the amount left in may be very considerable. Conversely, the celluloid takes up its charge comparatively tardily. If, for instance, an attempt is made to determine the capacity of the sheet, when in the mercury apparatus, by the simple discharge method, an eye which is accustomed to watching the "throw" of the galvanometer will at once observe that the needle is under the action of an extended discharge and not of a sudden impulse. When first this phenomenon was observed I carried out the following experiment:—The celluloid was charged from 20 cells for 15 seconds. It was then discharged, not through the galvanometer, but through the short-circuit key. After two seconds the short-circuit key was opened, and there was a discharge of a few degrees to the right—that is, in the "discharge" direction; this fell in a few seconds across the zero to 5 divs. on the left, where it remained perfectly steady. This curious reversal of sign was at first rather puzzling; if the spot had merely fallen to zero, it would have been easy to refer it to complete loss of charge; if it had fallen a little to the right of zero, it could have been attributed to incomplete loss of charge; but falling, as it did, on the negative side of zero, a novel case was presented.

After several repetitions, charging with various potentials up to as high as 900 volts, this reversal still manifested itself, although the time required to attain it was of course greater as the testing-voltage increased. Days and nights of short-circuiting would not wipe it out; whatever was tried, it remained always the same negative deflexion. It is, in fact, an initial permanent E.M.F. of about ·0006 of a volt with which nothing seems to interfere. It is apparently due to the contact of the mercury with the celluloid ; it did not appear when metallic plates were used. This point having been so far settled, the experiments on slow discharge were repeated with 100, 200, 400, and 600 cells ; the corresponding discharge-readings—after short-circuiting the sheet for two seconds in each case before discharge—were respectively 18, 36, 57, and 80 divs., falling to zero, or very nearly to zero in a few minutes, and ultimately crossing the zero to −5. The discharge from a standard microfarad charged to 30 volts is 11,103 scale-divs. The instantaneous discharge from the celluloid sheet (5½ in. diam., ·00615 inch thick) with the same voltage, was 115 divs., which is the mean of the two readings obtained by reversing the battery. The test can scarcely be regarded as a capacity test under the above conditions. It is recorded here simply to show the phenomenon of slow discharge, and the existence of the permanent initial E.M.F.

### *Gutta-percha.*

Appended are the results of some tests upon a sheet of pure gutta-percha, in the mercury apparatus, at high voltages. The thickness of this sheet was about 2 mils ; the diameter of the circular mercury surface in contact with it, bounded by the insulating rings, was, as before, 5½ inches. Curves drawn from the tabulated results exhibit the phenomenon of dielectric hysteresis, and show that the effect of the current, up to a certain point, is to increase the resistance ; there is a subsequent tendency in the opposite direction, which would probably end in the breaking-down of the sample. There was no initial electromotive force to be observed with the gutta-percha.

Four separate tests were made upon the sheet, two with a cycle commencing at maximum volts, and two commencing at the minimum. In each case, whether beginning at the maximum or minimum volts, there was a decided increase of resistance as the result of a cycle. With such a thin sheet as 2 mils the test was a very severe one for the gutta-percha ; hence it is not surprising that the curves are somewhat broken. Two-thousandths of an inch of material is here effectively contending against 1200 volts, and setting up a barrier of 3000 million ohms over an area of 5½ inches.

A very interesting point about these four tests is that when the cycle commences at maximum voltage the subsequent readings are far steadier, and the curve of resistance and voltage smoother, than when minimum volts are started with; this is clearly indicated by a comparison of the four curves which may be drawn from these tables.

There is no absolute need to short-circuit the apparatus in order to remove the residual charge of the sheet; but short-circuiting probably quickens the process. This is a matter for further experiment. It was found that the sample of gutta-percha completely lost its charge after twenty-four hours, whether short-circuited or not, and during that time it regained its normal condition as regards insulation resistance. Twenty-four hours was therefore allowed between each of the four tests upon the gutta-percha sheet. As a rule, about ten minutes' rest was given between the consecutive voltages of individual tests; this was found to be time enough to practically discharge the sheet when short-circuited.

TABLE V.—Gutta-percha sheet ($G_2$).
(Volts *increasing*.)

| | volts 150 | volts 300 | volts 450 | volts 600 | volts 750 | volts 900 | volts 1050 | volts 1200 |
|---|---|---|---|---|---|---|---|---|
| $1^m$ … | 26·2 | 49·8 | 68·4 | 82 | unsteady<br>130 | unsteady<br>150 | unsteady<br>160 | steadier<br>171 |
| $2^m$ … | 25·6 | 47·6 | 65·0 | unsteady<br>98 | 117 | 135 | 160 | 159 |
| | $2272^{\frown}$ | $2384^{\frown}$ | $2614^{\frown}$ | $2910^{\frown}$ | $2290^{\frown}$ | $2383^{\frown}$ | $2602^{\frown}$ | $2789^{\frown}$ |

| | volts 1050 | volts 900 | volts 750 | volts 600 | volts 450 | volts 300 | volts 150 | volts 1200 |
|---|---|---|---|---|---|---|---|---|
| $1^m$ … | steady<br>126 | 100 | 73 | 53·5 | 38·5 | 24·5 | 12·0 | 170 |
| $2^m$ … | 126 | 100 | 75 | 49·0 | 31·0 | 18·0 | 9·2 | 148 |
| | $3303^{\frown}$ | $3572^{\frown}$ | $4079^{\frown}$ | $4459^{\frown}$ | $4645^{\frown}$ | $4845^{\frown}$ | $4961^{\frown}$ | $2805^{\frown}$ |

Temp. =66° F.

### TABLE VI.—Gutta-percha sheet ($G_2$).
(Volts *diminishing.*)

| | volts 1200 | volts 1050 | volts 900 | volts 750 | volts 600 | volts 450 | volts 300 | volts 150 |
|---|---|---|---|---|---|---|---|---|
| 1m ... | steady<br>171·2 | 137·6 | 112·5 | 91·8 | 71·8 | 54·2 | 39 | 20·0 |
| 2m ... | 166·0 | 135·0 | 111·5 | 89·5 | 68·0 | 49·0 | 34 | 17·7 |
| | 3220^ | 3510^ | 3670^ | 3760^ | 3840^ | 3820^ | 3530^ | 3470^ |

| | volts 300 | volts 450 | volts 600 | volts 750 | volts 900 | volts 1050 | volts 1200 |
|---|---|---|---|---|---|---|---|
| 1m ... | 38·5 | 53·5 | 69·5 | 84 | 100 | 118·5 | steady<br>145 |
| 2m ... | 33·8 | 48·0 | 64·5 | 81 | 98 | a little unsteady<br>119·0 | 143 |
| | 3570^ | 3870^ | 3970^ | 4130^ | 4130^ | 4070^ | 3800^ |

23rd April, 1894. Temp. =64°·5 F.

### TABLE VII.—Gutta-percha sheet ($G_2$).
(Volts *increasing.*)

| | volts 150 | volts 300 | volts 450 | volts 600 | volts 750 | volts 900 | volts 1050 |
|---|---|---|---|---|---|---|---|
| 1m ... | 22·0 | unsteady<br>74 | unsteady<br>85 | steady<br>84·5 | steady<br>100·0 | unsteady<br>118·2 | unsteady<br>143 |
| 2m ... | 21·6 | 54 | 71 | 80·5 | 94·5 | 118·0 | 139 |
| | 2960^ | 1730^ | 2280^ | 3050^ | 3230^ | 3260^ | 3140^ |

| | volts 1200 | volts 1050 | volts 900 | volts 750 | volts 600 | volts 450 | volts 300 | volts 150 |
|---|---|---|---|---|---|---|---|---|
| 1m ... | unsteady<br>167 | 154 | 125 | 96·5 | 70·5 | 52·5 | 34·0 | 16·6 |
| 2m ... | 193 | 152 | 123 | 96·0 | 67·0 | 44·2 | 27·5 | 14·6 |
| | 3070^ | 2920^ | 3080^ | 3350^ | 3660^ | 3690^ | 3760^ | 3920^ |

24th April, 1894. Temp. =63° F.

TABLE VIII.—Gutta-percha sheet ($G_2$).
(Volts *diminishing.*)

| | volts 1200 | volts 1050 | volts 900 | volts 750 | volts 600 | volts 450 | volts 300 | volts 150 |
|---|---|---|---|---|---|---|---|---|
| 1m ... | 231 | 143 | 99 | 68 | 50·0 | 37 6 | 25·8 | 13·0 |
| 2m ... | 187 | 131 | 94 | 65 | 48·7 | 35·6 | 24·0 | 12·3 |
| | 1620^ | 2290^ | 2830^ | 3430^ | 3720^ | 3700^ | 357 | 3550^ |

| | volts 300 | volts 450 | volts 600 | volts 750 | volts 900 | volts 1050 | volts 1200 |
|---|---|---|---|---|---|---|---|
| 1m ... | 25·6 | 37·4 | 47·0 | 58 | 73 | 91 | 109 |
| 2m ... | 23·8 | 34·6 | 44·5 | 58 | 75 | 92 | 117 |
| | 3300^ | 3720^ | 3970^ | 4020^ | 3780^ | 3600^ | 3430^ |

25th April, 1894. Temp. =62° F.

The small opaque white spots, observed within the celluloid under the microscope, led to some further experiments to investigate the effect of isolated foreign particles within the substance and upon the surface of dielectrics. Coarse brass filings were scattered as thickly as possible over one face of a warmed strip of gutta-percha, 16 inches long, 2 inches wide, and ¼ inch thick. The insulation of such a strip is not exactly what might be expected; when tested even with 750 volts its resistance was practically infinite, and was certainly greater than 600,000 megohms. A charged gold-leaf electroscope could not be discharged with such a strip in this condition. If, however, a wet cloth was passed once over the non-metallic face of the strip, or if it was simply breathed upon, the insulation fell to 5000 megohms, and the strip now easily discharged the electroscope. A round rod of gutta-percha can be warmed and rolled in a heap of brass filings so as to appear almost like a brass rod, and such a rod does not discharge the electroscope. This would be an instructive experiment for schools and instrument-makers.

### "*Sensitive*" *Dielectrics.*

The next experiments were made with rods formed of a mixture of gutta-percha and brass filings melted together in various proportions. The length of these rods was about 20 inches, and their diameter ¾ of an inch. Contact was made with the ends for about 1½ inch by tin-foil which was bound round with wire. It is found that, for small proportions of brass filings, the resistance between the ends of these rods is exceedingly high, and this high resistance is maintained until about 2 parts, by weight, of brass are mixed with one part, by weight, of gutta-percha. Here a "critical" point of proportionality between the two substances occurs, *under* which the rods have a very low resistance, of something like one ohm; and *above* which the resistance is exceedingly high, and can only be measured in megohms. Several rods were made at or near this "critical" point, and in no case could a medium resistance of, say, a few hundred ohms be attained. All the rods were either of very high or very low resistance.

The method of making them is to warm a sheet of gutta-percha upon a hot plate, using French chalk to prevent sticking. The filings are sprinkled in as soon as the sheet becomes soft. The whole is then made up into a pudding, which is again flattened out into a sheet; this is repeated until a good mixture is arrived at. The compound is then rolled into rods.

Table IX. gives the proportion by weight of these rods and the corresponding resistance. When rods made up in this way are submitted to the action of oscillating discharges, they behave in a similar manner to the "impulsion" cells of Prof. Minchin and the tubes of M. Branly. If, for instance, one of the low-resistance rods of, say, four parts by weight of gutta-percha to nine of brass filings is connected to one arm of a Wheatstone's bridge and balanced, an oscillatory discharge made anywhere near it will, in nearly all cases, produce a considerable diminution of resistance—in some cases amounting to more than 10 per cent., and, in one experiment, to as much as 45 per cent. This charge remains until restored to the former condition of things by a slight mechanical tap. I have repeated this experiment upon seven different rods,

Table IX.

| No. of Rod. | Proportion by weight $\frac{\text{G.P.}}{\text{Brass}}$. | Approximate Resistance. |
|---|---|---|
| 1 | $\frac{1}{2}$ | ·2 ohm. |
| 2 | ? | ·07 ,, |
| 3 | $\frac{1}{3}$ | ·11 ,, |
| 4 | $\frac{1}{1}$ | ∞. |
| 5 | $\frac{2}{1}$ | ∞. |
| 6 | $\frac{2}{3}$ | 283,000 megohms. |
| 7 | $\frac{4}{7}$ | 173,000 ,, |
| 8 | $\frac{1}{2}$ | ∞. |
| 9 | $\frac{1}{2}$ | 770 megohms. |
| 10 | $\frac{1}{3}$ | ·37 ohm. |
| 11 | $\frac{2}{5}$ | 1·68 ,, |
| 12 | $\frac{1}{2}$ | 19 ohms. |
| 13 | $\frac{4}{9}$ | 3·9 ,, |
| 14 | $\frac{4}{11}$ | ·48 ohm. |
| 15 | .... | 1·5 megohm. |

and have, in each case, obtained a diminution when the discharge-spark passed at the oscillator. The small-resistance rods of Table IX. were all sensitive to these electromagnetic oscillations. The high-resistance rods do not come within the range of measurement of the usual form of Wheatstone's bridge; the ordinary insulation-test was therefore applied, using a battery of 400 Leclanché cells. In this way resistances up to 600,000 megohms could be measured. A rod composed of 4 parts, by weight, of gutta-percha, to 7 parts of brass filings had practically infinite resistance. Another, having 2 parts, by weight, of gutta-percha to 3 of brass, had 100,000 megohms. A third, made up in the ratio of 4 parts gutta-percha to 7 of brass, was of infinite resistance. Four rods were made in the proportion 1 gutta-percha to 2 of brass, which is near the critical ratio of conductor to insulator; their resistances were, respectively, ∞, 40 megohms, and 12 ohms. The ·17-ohm rod exhibited a decided, but not very great diminution of resistance under the influence of the oscillator. Apparently, the high-resistance rods are unaffected by the discharges. The 40-megohm rod was not of very constant resistance, the spot moved up and down the scale; the spark had therefore to be passed at moments when the spot halted,—the result was not very satisfactory. At one time it was thought actually to *increase* the resistance of this rod. The 12-ohm rod was especially interesting from its extreme sensitiveness; in one condition it had a resistance of 19 ohms, the sudden passage of a spark at the oscillator reduced this by 45 per cent. The rod was generally unstable. The 40-megohm rod seemed the one most nearly corresponding, in its galvanometer-readings, with a faulty cable; the readings being erratic. Its resistance has, at times, been as high as 770 megohms. This rod is probably unstable in some opposite direction to the 12-ohm rod; they were both made in the same proportions and in the same manner. In Table IX. they appear as No. 9 and No. 12 respectively.

### *Alternating Voltages.*

Tests were now made upon specimens submitted to alternating currents, and I have to thank Mr. George Bousfield for assisting me in this part of the experiments. I took the strip sprinkled with filings, and two rods; these were first tested for insulation in the ordinary way, with the following results:—

| Dielectric. | Resistance. |
|---|---|
| Strip = | ∞. |
| No. 6 = | 283,000 megohms. |
| No. 9 = | 47·2 megohms. |

The strip began to break down under the action of the alternating current at 900 volts; at 3000 volts it was emitting small local arcs, some crimson, others violet. After the application for some time of this high voltage the number and brilliancy of the arcs diminished,—the insulation had apparently improved. At 5500 volts there were bright discharges similar to the first. These were not of the nature of long sparks, but of small local arcs.

Rod No. 6 gave way at 6500 volts and exhibited the same apparent improvement in insulation. The arcs shot out in miniature flames, like very small blowpipe blasts; locally, as in the case of the strip.

With rod No. 9 sparking commenced at 1500 volts, having the appearance of small beads of crimson and violet light burning themselves out at fixed points. When these specimens had become cool their insulation was again tested.

| Dielectric. | Resistance. |
|---|---|
| Strip = | $\infty$. |
| No. 6 = | 70,750 megohms. |
| No. 9 = | 2020 megohms. |

The strip thus appears to have recovered entirely. No. 6 has fallen to a quarter of its first value, and No. 9 has greatly improved, under this trying ordeal.

Rod No. 15 was compounded of iron filings, Sr, &c., with a view to obtaining a brilliant discharge. The salts brought the insulation down rather low; there was a great deal of heat generated, and little else. Such a rod should probably be made simply of metallic powders intermixed with the dielectric.

## Discussion.

Mr. Enright asked questions as to the electrification of gutta-percha, and the bridge-connexions in the resistance tests of the semi-conducting rods respectively.

Mr. Charles Bright said the curious phenomenon, in Mr. Appleyard's experiments, of the dielectric resistance of gutta-percha strip remaining much the same when brass filings were pressed on to its surface, is, of course, most interesting. These filings, as I understand, had no appreciable effect electrically until a certain quantity were incorporated, when the resistance suddenly broke down and, in fact, soon gave good conduction. The explanation of this fact is presumably that as long as the metal filings are not sufficiently closely packed to be touching one another, they take no material part in the conduction of electricity through the gutta-percha, but when once they touch one another sufficiently closely, the conduction (or resistance) of the gutta-percha sheet becomes practically that of the brass.

# XVII. *Note on the Behaviour of certain Bodies in presence of Electromagnetic Oscillations.* *By* Prof. G. M. MINCHIN, *M.A.*[*]

THE question of the employment of impulsion-cells, metallic films, and bodies of similar behaviour, for detecting the nodes &c. of electromagnetic vibrations, has frequently been raised; and the reading of Mr. Appleyard's paper on rods formed of a mixture of gutta-percha and metallic filings offers an opportunity for a few remarks on the subject.

So far as experiment has gone hitherto, it does not seem possible to use these bodies for detecting nodes; and the reason is simply this—that the physical states of the bodies in question are too variable to admit of the observation of any constant *régime.*

I have lately made a few observations on films and metallic surfaces formed by imbedding fine metallic powders in thin layers of gelatine, shellac, and sealing-wax spread on plates of glass, in continuation of the work described and experimentally illustrated at a previous meeting of the Physical Society; and the results are, briefly, as follows:—If we put in the circuit of a battery and a galvanometer a surface formed by fine metallic powder imbedded in a layer of sealing-wax, we find that this surface (although, to the eye, a continuous surface of metal) is a non-conductor. Indeed, if the electrodes connected with this surface are also connected with an electrometer, we find that this surface has an *infinite* resistance. Now if feeble electromagnetic oscillations are produced in the neighbourhood of the non-conducting surface, it will refuse to respond and remain a non-conductor. Let the field round the surface be greatly increased, or let one of the electrodes be actually touched by a charged body: then the surface becomes a conductor. Let its conductivity be now destroyed (by breaking the contact of the surface with the electrode, for example, as described in my previous paper), and it will be found after this to respond very

[*] Read as part of the discussion on Mr. Appleyard's paper on Dielectrics, May 11, 1894.

easily to the actions which previously produced no effect upon it. In other words, *once we have succeeded in driving a current through the metallic-powder surface, it responds to very feeble electromagnetic impulses, whereas it previously failed to respond to strong impulses.*

When the contact of the surface with the electrode is broken and then almost instantly re-made, the behaviour of the surface depends on certain things. Firstly, if the metal powder forming the surface is embedded in gelatine which retains some plasticity, the breaking of the contact is fatal to the conductivity of the surface : the surface rapidly reverts to the non-conducting state. Secondly, if the substratum of the metallic powder is a hard substance like sealing-wax, and if the electromagnetic impulses received by it have been strong, the surface will remain a conductor for a long time—possibly for 24 hours or more. But if the impulses to which it has been subjected have been small, and the conductivity consequently small, the surface rapidly reverts to the non-conducting state, less than a minute's breaking of contact sufficing to re-establish insulation.

Again, surfaces with a hard-set substratum (like sealing-wax) are scarcely, if at all, sensitive to mechanical impulses.

A series of experiments made with a particular surface gave this as an almost invariable result—if the surface is in the non-conducting state, and a feeble electromagnetic field is produced round it, it becomes a conductor ; but if, while it is conducting, a strong field be produced round it, its conductivity is destroyed. I have no doubt that a law of this kind holds for all such bodies ; the nature of the change produced in them depends either on the amplitudes or on the frequencies of the incident impulses ; but, in order to verify it, we should be able to deal with a film which from a definite state of non-conductiveness changes always to a definite state of conductivity ; and this has been, so far, impossible.

It may be well to give a numerical illustration of the change of resistance produced in a film. Thus, when the electrodes touching a tin-powder surface were two platinum wires the extremities of which were rounded in an oxy-hydrogen flame, and the length of the film in a right line between them was about 1 centim., the resistance of the surface varied from ∞ to about 130 ohms. This resistance was measured by connecting the poles of a quadrant electrometer with the above platinum electrodes, while the current of two Leclanché cells was passing through the galvanometer and metallic surface, and reading the difference of potential indicated by the electrometer.

Of course this assumes that no E.M.F. is set up in the film by the electric impulse which rendered it a conductor—an assumption the truth of which was verified by using a key which suddenly threw the battery out of circuit and inserted the electrometer instead. Not the slightest E.M.F. in the film could be detected.

I must, however, repeat what I have previously stated concerning the nature of an impulsion-cell—viz., that, while in the case of films and M. Branly's tubes of metallic filings the whole phenomenon relates merely to changes of resistance, this is not the case for an impulsion-cell. The current of a single Minotto can pass through the impulsion-cell both in its state of insensitiveness to light and in its state of sensitiveness.

It may be natural to conjecture that iron powder might present some striking difference from those of other metals; but, forming surfaces with the magnetic oxide of iron, I was not able to detect any special characteristic of such surfaces.

The behaviour of all these bodies in very weak fields and in very strong ones is a matter which requires working out.

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## XVIII. *The Passage of Hydrogen through a Palladium Septum, and the Pressure which it produces.* *By* WILLIAM RAMSAY, *F.R.S.*

IT has been frequently cited as an argument in favour of attributing the osmotic pressure exercised by a substance in dilute solution on the walls of a vessel permeable to the solvent but not to the dissolved substance, that if a vessel were constructed of palladium, which, as Graham's researches showed, is permeable to hydrogen, but not to many other gases, such a vessel would be subjected on its interior walls to a high pressure if it were filled with an indifferent gas and exposed on its exterior to an atmosphere of hydrogen. The gas confined in the vessel, not being able to escape, would exert the pressure at which it was allowed to enter; while the interior of the vessel would be a vacuum to hydrogen; and as its walls are permeable to hydrogen, pressure should rise by passage of hydrogen into the interior, until the pressure of the hydrogen on the interior walls became equal to that on the exterior walls. The effect of this would be to superadd the pressure of the hydrogen to that of the gas originally contained in the vessel; and if it be supposed that the vessel was originally filled at atmospheric pressure, the entry of hydrogen should increase that pressure by another atmosphere, providing the hydrogen surrounding the exterior walls of the vessel be at atmospheric pressure.

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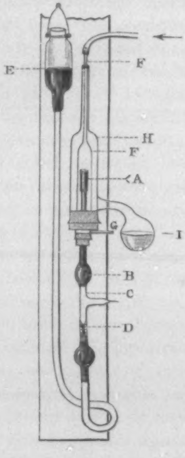
* Read May 25, 1894.

It has been suggested that when pressure is raised by the passage of water into the interior of a cell with semipermeable walls containing a solution, the rise of pressure is due, not to the pressure exercised by the molecules of the dissolved substance, but to that produced by the entering water. Gases present us with an exact analogy. It is idle to inquire what causes the rise of pressure in the interior of such a palladium "cell." The total pressure is due to the hydrogen and to the gas with which the cell was originally filled; the original pressure has undoubtedly been increased by the entry of hydrogen. But a portion of the pressure—and the effective portion, from the point of view of osmotic pressure—is due to the original gas, whether nitrogen, carbon dioxide, or any gas whatever to which the cell-walls are impervious, and which is not chemically attacked by hydrogen. It is therefore quite correct to ascribe osmotic pressure to the dissolved substance, although it is apparently produced by entry of solvent.

The experiments to be described were made with the object of submitting this entry of hydrogen through the walls of a palladium cell to quantitative study. After considerable progress had been made, a paper by A. Biltz (*Zeitschr. f. phys. Chem.* ix. p. 152) was published, describing lecture-experiments devised to show the ordinary diffusion of gases without a septum, diffusion with a leaky septum of porous earthenware, and also diffusion with a semipermeable septum, permitting the passage of hydrogen, but hindering the passage of other gases. Biltz employed for the last-mentioned purpose an iron tube, and made a few rough quantitative measurements; but he does not appear to have continued any experiment long enough to obtain a maximum pressure, nor was his apparatus designed with the object of quantitative measurement, but only for the purpose of class demonstration.

### *Description of Apparatus.*

The apparatus which was employed is represented in the accompanying woodcut.



AB is a tube of platinum, the top portion of which, at A, is of palladium and closed at its upper end. At B the platinum tube is sealed or cemented on to a glass tube C, with a lateral branch, represented in the figure as drawn off and closed. Somewhat lower down, the tube is sealed to a capillary D, on which graduations are etched. The tube then widens to a bulb, and is finally connected by thick flexible tubing to a reservoir of mercury E.

The palladium tube is surrounded by a glass tube F, also provided with a lateral exit at G, and fitting tightly into a jacket H, which may be heated by boiling the liquid in the bulb I. A gas, passed in at F, would thus surround the palladium tube and escape at G; or if heavier than air, if introduced at G it would escape at F. The palladium cell could be heated to any desired temperature by choosing an appropriate jacketing vapour. The whole apparatus stood in front of a glass mirror-scale, on which the level of the mercury at D and E could be read off. It was possible to read to one tenth of a millimetre, but such accuracy of reading was generally unnecessary.

### *Description of an Experiment.*

A clip was placed on the india-rubber tube joining D and E, and the side-tube C, which at this time was open, was connected with a reservoir of some gas, *e. g.* of nitrogen, by means of a three-way tap. The palladium tube was pumped empty, and then filled with dry nitrogen ; the operation was repeated ten times, so as to ensure absence of air. The nitrogen was finally allowed to enter the apparatus under slight pressure, and the side-tube C was sealed. The liquid in I was then boiled so as to jacket the tubes F and A, and the clip on the india-rubber tube was opened. When the temperature had become constant, the reservoir of mercury E was brought approximately to a level with a mark on the capillary tube D, and the capillary tube at C was broken. Gas then escaped through C until the pressure in the tube A became equal to that of the atmosphere. The capillary point was again sealed. An accurate reading was then taken, the mercury reservoir being placed so that an exact volume of gas was contained in the palladium cell under a known pressure.

Hydrogen carefully purified by washing with potassium permanganate, silver nitrate, and caustic potash, and dried by passage through sulphuric acid and over phosphorus pentoxide, was then passed in through the tube F, escaping at G. Pressure rapidly rose in the interior of the apparatus, and was measured by raising the mercury reservoir. When it had attained its maximum a reading was taken, the position of the mercury in the capillary stem being so adjusted that the capacity of the cell was accurately the same as at the commencement of the experiments. The difference between the initial and final pressure is due to entry of hydrogen.

The success of such experiments depends on the condition of the palladium. After having been used once or twice the interior of the palladium tube became coated with mercury, even although the level of mercury (which was cold) lay far below the palladium top. It appears that palladium absorbs mercury-vapour with avidity, thus rendering the palladium cell a partial vacuum to mercury-vapour. Vapour rises from the cold mercury to restore pressure, and is again absorbed. It was therefore necessary to heat the palladium tube after each experiment in order to expel mercury. This had the effect of oxidizing the palladium and of covering it with a brownish-black film. To remove the oxide, the tube was made the negative pole of a battery, and dilute sulphuric acid was electrolysed, both on the inside and outside of the palladium tube. It was then dried at a low temperature; the external surface was polished with a little dry emery; the tube was cemented into its place, and was ready for a fresh experiment. Without such precautions the passage of hydrogen is very slow and incomplete. It should be mentioned that before commencing an experiment it was necessary to jacket the palladium tube at 220° and to pass a current of air over it for some time. In this way the combined hydrogen was removed; hydrogen escaped from the exterior of the tube and was replaced by air or some other gas in the interior.

### *Account of Experiments.*

The experiments admit of classification under five heads:—

1. Experiments with the tube filled with air.
2. Experiments with the tube filled with nitrogen.
3. Experiments in which the hydrogen passed over the exterior of the tube was diluted with nitrogen or other gases, when it exercised only a partial pressure on the exterior walls of the tube.
4. Experiments in which the palladium tube was filled with other gases.
5. Experiments with a nickel tube and carbon monoxide.

*Experiment* 1.—The tube was filled with air and jacketed with bromonaphthalene, boiling at about 280°. The barometric pressure during the experiment was constant at 743·1 millim. On passing hydrogen for three hours the pressure in the palladium cell had become constant; the rise of pressure was 573 millim.

Water appeared on the surface of the mercury in the capillary tube, showing that the hydrogen had combined with the oxygen of the air. The rise of pressure measured should therefore have been that of the nitrogen remaining in the cell, viz 585 millim.

It may be concluded, then, that hydrogen combines with oxygen in presence of palladium at 280°, and that the residual nitrogen exerts nearly its partial pressure; or, as will be afterwards shown to be a more correct statement, the nitrogen exerts its full partial pressure, and the hydrogen in the interior exerts a large fraction of the pressure of the external hydrogen.

*Experiment* 2.—The tube was filled with pure dry nitrogen, and exposed to hydrogen, as before, at the same temperature. The pressure, after it had become fairly steady, was 703·2 millim in excess of that of the atmosphere (748·1 millim.). The hydrogen was next removed by passing a current of air over the exterior of the tube, and the pressure was again raised by a current of hydrogen. After about three-quarters of an hour the pressure was 699·8 millim. in excess of that of the atmosphere, a quarter of an hour later it was 721·1 millim., and in another quarter of an hour it had risen to 733·0 millim. It appeared then to be stationary. The barometric pressure was still 748·1 millim.; it therefore appears that the pressures of the hydrogen on the exterior and interior of the palladium tube were nearly equal.

It was noticed during these experiments that when the gas was changed the pressure invariably fell a little on admitting hydrogen and rose a little on admitting oxygen; the direction of the pressure then changed, and the usual rise with hydrogen and fall with air occurred. I think that this is to be attributed to the fact that the palladium vessel increases its capacity suddenly on exposure to hydrogen, and decreases it on exposure to air after having been exposed to hydrogen. But the total change of volume is a very minute one; it is noticeable only by the rise or fall of the mercury in the capillary tube to the amount of one or two millimetres; and the total change of volume is certainly less than 0·1 per cent. of the capacity of the vessel.

*Experiments* 3, 4, *and* 5.—The next three experiments gave readings much lower than those previously obtained. The barometric reading was 748·6 millim. The rise in experiment 3 was 650·3 millim.; in experiment 4, 654·2 millim.; and in experiment 5, 657·8 millim.

This led me to suspect that the palladium tube had undergone alteration. It was therefore disconnected and cleaned as before described. It was finally filled with nitrogen.

*Experiments* 6, 7, 8, 9, *and* 10.—The barometric pressure was 770·2 millim. The final pressure in experiment 6 was 698·5; in 7, 692·1; in 8, the barometric pressure being 768·8 millim., the final pressure was 686·4 millim. In experiment 9, with a barometer-reading of 762·2 millim., the reading was 692·4 millim.; and in 10, the barometer-reading being 759·2, the pressure was 688·4 millim.

To summarize these results it is necessary to compare the pressure of the internal hydrogen with that of the external hydrogen. The following table gives their ratios :—

| Experiment. | (1) | (2) | (3) | (4) | (5) |
|---|---|---|---|---|---|
| Ratio . . . . | 0·9400 | 0·9798 | 0·8687 | 0·8739 | 0·8780 |

| Experiment. | (6) | (7) | (8) | (9) | (10) |
|---|---|---|---|---|---|
| Ratio . . . . | 0·9069 | 0·8986 | 0·8928 | 0·9084 | 0·9067 |

These results do not exhibit any great degree of constancy, but I am sure that their difference depends largely, if not wholly, on the state of the surface of the palladium. The mean result is 0·9053, a number closely approximating to the last five determinations. This would lead to the conclusion that the pressure of the internal hydrogen rises to rather more than $\frac{9}{10}$ of the pressure of the external hydrogen at 280°.

*Experiment* 11.—The temperature was now kept at the boiling-point of quinoline (about 237°). The passage of hydrogen through palladium is so slow at this temperature that patience failed me to make more than one determination. It was begun on May 4th. On May 10th pressure was still rising, but very slowly. On May 11th it had reached 501·7 millim.; on the 13th it was 525·2 millim., and on the 14th 531·2 millim. Taking the figure actually read, the fractional pressure (barometer = 766·3 millim.) was 0·6932. Judging from this experiment, the pressure would appear to depend on the temperature of the palladium and of the hydrogen. Still, it is possible that had the experiment been carried on sufficiently far, the pressure might have risen much higher.

*Experiment* 12.—The next set of experiments was made at a higher temperature—that of the boiling-point of dibenzylketone (335°). The pressure registered at a barometric height of 758·7 millim. was 681·6 millim. The ratio is 0·8984, practically identical with that obtained at the boiling-point of bromonaphthalene.

*Experiments* 13, 14, *and* 15.—The hydrogen in these experiments was mixed with 50 per cent. of nitrogen, so that the exterior of the palladium tube was exposed to a partial pressure of hydrogen. The first of this set gave a pressure of hydrogen of 367·9 millim., the barometer standing at 770·9 millim.; the second, 352·9 millim., barometer at 771·8 millim.; and the third 362·7 millim. at the same pressure.

*Experiment* 16 was made with a mixture of one volume of hydrogen to three of nitrogen; the read pressure was 176·7 millim., the barometric height being 756·5 millim.

The ratios are:—

| Experiment. | 13 | 14 | 15 | |
|---|---|---|---|---|
| Ratio . . . . | 0·4771 | 0·4573 | 0·4700. | Mean 0·4681. |

Experiment 16: Ratio 0·2336.

Multiplying the first mean ratio by 2, and the second by 4, the products are comparable with that from pure hydrogen. The figures are:—

| | |
|---|---|
| Pure hydrogen . . . . . . . . . | 0·9053 |
| Hydrogen + 50 p. c. nitrogen . . . | 0·9362 |
| Hydrogen + 75 p. c. nitrogen . . . | 0·9544 |

The pressure, as might have been anticipated, is proportional to the partial pressure of the external hydrogen.

It is obviously possible to test the percentage of hydrogen in coal-gas by this means, provided the other constituents of coal-gas are unable to pass through palladium. An experiment with marsh-gas showed that it is not capable of permeating palladium; and the vapour of ether is also unable to pass.

*Experiments* 17 *and* 18.—At 280° the pressures with a sample of London coal-gas were 364·4 millim., at a barometric pressure of 760·4 millim.; and 361·8 millim. at a barometric pressure of 761·5 millim. The ratios are 0·4792 and 0·4751 respectively. Supposing the highest attainable ratio to be

0·9053, as deduced from the ten experiments with pure hydrogen, the percentage of hydrogen is easily found by the ratios (0·4792 × 100)/0 9053, and (0·4751 × 100)/0·9053. The numbers are 52·94 and 52·49 per cent. respectively. It would be possible thus to have a continuous register of the percentage amount of hydrogen in coal-gas, provided the palladium did not alter its state. As it is, I am afraid that the apparatus will not retain its activity for a sufficiently long time. It should also be remarked that it is necessary to wash the coal-gas with a solution of potassium permanganate, in order to free it from sulphur compounds. If this precaution is not taken, the palladium becomes coated with a layer of sulphide, and it ceases to be permeable to hydrogen.

Experiments were next made in which the palladium tube contained various gases.

*Experiment* 19.—The tube contained carbon dioxide. On exposing it to hydrogen at 280° the pressure rose with great rapidity—much more rapidly than had previously been observed. The rise ceased at 735 millim., the barometric pressure being 764·0. The quotient is 0·9621, a higher number than any yet obtained.

*Experiment* 20.—Carbon monoxide was in the interior; the pressure rose rapidly on admission of hydrogen to 734·5 millim., the barometer reading 769·5. The quotient is 0·9545, also a very high number. In both of these experiments the fall on passing air over the exterior of the tube was much slower than the rise with hydrogen. The end point was difficult to note, for the last change of pressure was very slow. It may be that the exterior surface of the palladium being exposed to hydrogen alone, little difficulty was experienced in molecules entering; but that on reversing the action, the contact of hydrogen with the interior walls was interfered with by the indifferent gas present. The same phenomenon had previously been noticed, but in a minor degree. It is noteworthy that no trace of water was formed in either case. Hydrogenized palladium is without action on carbon monoxide or dioxide at 280°.

*Experiment* 21.—The tube was filled with cyanogen. The total pressure was 741 millim., the barometer standing at 764·5 millim. The quotient is 0·9693, a very high number.

On substituting air, the cyanogen exerted finally a pressure of 740 millim. This would appear to indicate that palladium is quite impermeable to cyanogen, and is not attacked by it at 280°.

*Experiment* 22.—Nitric oxide was introduced into the tube, at a barometric pressure (corrected) of 765 millim. On passing hydrogen the pressure rose 368 millim.; the total pressure of the gases in the tube was 368 + 763 = 1131 millim., the barometric height being 763 millim. The increase of pressure was therefore 1131 − 765 = 366 millim. Supposing that the nitric oxide had reacted with the hydrogen, forming nitrogen and water, thus:—

$$\underset{\text{4 vols.}}{2NO} + 2H_2 = 2H_2O + \underset{\text{2 vols.}}{N_2},$$

the pressure of the nitric oxide would have been halved, and would have amounted to 765/2 = 382·5 millim. But it is to be supposed that the resulting water would have exerted its usual vapour-pressure; and as its temperature was 22°, the pressure of the water-vapour would be 18·5 millim.

We have thus:—

| | | millim. |
|---|---|---|
| Pressure of $H_2+N_2+H_2O$ vapour . | 368 + 763 | = 1131 |
| Pressure of $N_2+H_2O$ vapour . | 382·5 + 18·5 | = 401 |
| Hence pressure of hydrogen alone | | = 730 |

and the quotient 730/765 = 0·9543, a number almost identical with those previously obtained.

*Experiment* 23.—A similar experiment was made with nitrous oxide. Here, too, reduction occurs at 280°; but the volume of the residual nitrogen is equal to that of the nitrous oxide.

The initial pressure of the nitrous oxide was 772 millim. After passing hydrogen, the total pressure was 1489·5 millim. The difference, 717·5 millim., is to be ascribed to hydrogen and water-vapour. The barometer stood at 761 millim. Deducting 18·5 millim., the pressure of water-vapour at 22°, the pressure of the hydrogen alone is 699 millim. And the quotient 699·0/761 = 0·9186.

The hydrogen was then removed by a current of air on the external surface of the palladium. The pressure of the nitrogen was then 780·5 millim. Again restoring hydrogen on the exterior, the pressure rose to 727·5 millim., the barometric pressure being 761 millim. The pressure ascribable to hydrogen and water-vapour is thus 708 millim.; subtracting the pressure of water-vapour, 22·5 millim., the remainder, 685·5 millim., is due to hydrogen. The quotient is 0·9008. Here again a reasonable correspondence is found.

It is evident that in all cases the pressure of the hydrogen in the interior of the palladium tube is lower than the barometric pressure, *i. e.* lower than the pressure of the hydrogen on the exterior. It will be convenient here to tabulate the ratios found :—

| | | |
|---|---|---|
| *a.* | Mean ratio from hydrogen and nitrogen at 280° | 0·9053 |
| *b.* | Ratio at 335° | 0·8984 |
| *c.* | Ratio with 50 per cent. of hydrogen at 335° | 0·9362 |
| *d.* | Ratio with 25 per cent. of hydrogen at 335° | 0·9344 |
| *e.* | Ratio from hydrogen and carbon dioxide at 280°. | 0·9621 |
| *f.* | Ratio from hydrogen and carbon monoxide at 280° | 0·9545 |
| *g.* | Ratio from hydrogen and cyanogen at 280° | 0·9693 |

I omit the two last determinations, as uncertainty was introduced owing to the presence of water-vapour.

On reviewing these results, it would appear that the ratio is not altered by rise of temperature above 280°. The same number was obtained at 280° and at 335°. But at a lower temperature the ratio is much smaller, if, indeed, the end-point was really reached. Dilution of the hydrogen appears to raise the ratio ; and the presence of carbon dioxide, carbon monoxide, or cyanogen in the interior of the palladium tube appears to be favourable to the passage of hydrogen.

To what are these results to be ascribed ?

Troost and Hautefeuille have determined the pressures of dissociation of the definite hydride of palladium, $Pd_2H$ (*Compt. rend.* lxxviii. p. 686). At 130° the pressure is nearly equal to that of the atmosphere, it is 624 millim.; while at 140° the pressure is 812 millim. It rises rapidly with temperature, and at the highest temperature given, 170°, it amounts to the large number 1840 millim. It is impossible to believe, then, that any hydride of palladium should exist even at the lowest of the temperatures employed, 223°. Yet palladium becomes quickly permeable to hydrogen only at a higher temperature.

Two questions require answer :—(1) Why is palladium permeable to hydrogen? and (2) Why is the pressure of the internal hydrogen always less than that of the external hydrogen?

(1) It is hardly probable that the palladium acts simply as a filter, allowing small molecules of hydrogen to pass while blocking the passage of larger molecules of other gases. Graham, however, appears to regard this as in some measure the cause of the passage. His words are :—"Such phenomena of gaseous penetration appear to suggest a progression in the degree of porosity. There appear to be (1) pores through which gases pass under pressure or by capillary transpiration, as in dry wood and many minerals; (2) pores through which gases do not pass under pressure, but pass by their proper molecular movement of diffusion as in artificial graphite; and (3) pores through which gases pass neither by capillary transpiration nor by their proper diffusive movement, but only after liquefaction, such as the pores of wrought metals and the finest pores of graphite."

It is noteworthy that Graham considers that gases are liquefied in the pores of metals. But in the experiments here described this can hardly be the case. For at 270° and at higher temperatures hydrides of palladium do not exist, as is conclusively shown by Troost and Hautefeuille; just as water does not exist in superheated steam. And yet it is at these temperatures that palladium is permeable to hydrogen, and not at temperatures at which hydride of palladium is stable.

There are several facts which must be borne in mind in seeking for an interpretation for the phenomenon of the passage of hydrogen through palladium.

First. The hydrogen in the act of passing is a reducing agent, as shown by its behaviour towards the oxides of nitrogen. At such temperatures as were here employed, hydrogen is without action on the lower oxides of nitrogen.

Second. Bellati and Lussano have shown (*Atti R. Ist. Ven.* i. series vii. p. 1173) that hydrogen "diffuses" through an iron plate which is used as a negative electrode on electrolysing dilute sulphuric acid. Their observation has been confirmed and amplified by Shields (Chem. News, lxv. p. 195). Shields has shown that neither lead nor platinum nor palladium allow hydrogen to pass under similar circumstances, and experiments made by myself show that nickel does not allow carbon monoxide to pass at temperatures at which that compound is stable.

Third. Iron and platinum, as shown by Deville and Debray (*Compt. rend.* lvii. p. 965), are permeable at a red heat to hydrogen.

I think these considerations prove that it is necessary to add a fourth class to the three classes suggested by Graham. Graham's first class involves actual holes, that is, passages large in comparison with the molecular diameter; his second implies pores small compared with molecular diameter, but still greatly exceeding that diameter; his third class would be termed "solid solution" in the present state of our knowledge, *i. e.* when coal-gas passes through india-rubber, the latter dissolves the gas on the side exposed to it, while the gas evaporates from the other side, so as to render the pressure of the dissolved gas equal on both sides of the membrane. The case is precisely analogous to the passage of water through a semi-permeable diaphragm. But, in order that hydrogen may pass through iron, it must be in the state in which it is liberated by an electric current, or it must be hot. That hydrogen will not pass through palladium at the ordinary temperature appears to show that the compound of palladium and hydrogen has practically no dissociation pressure at ordinary temperature; otherwise the hydrogen would pass by solution, in the same manner as coal-gas passes through india-rubber, or water through a semi-permeable diaphragm. That it will not pass, even when liberated by an electric current on one side of the palladium membrane, shows that it at once enters into combination with the palladium, and is no longer *in statu nascendi*, to use a generally understood expression which is independent of theory. But that it passes through hot palladium appears to show that it is then in a state analogous to that of electrically liberated hydrogen.

It is known that electrified bodies are discharged if a flame burns in their vicinity. This may be attributed to the liberation of atomic oxygen in a kind of Grotthus chain. For it may be imagined that when a molecule of oxygen encounters the oxidizable matter of a flame, it is dissociated: while one atom serves to oxidize the carbon, the other exchanges with a neighbouring molecule, and a succession of exchanges occur till the atomic oxygen near the electrified body receives or communicates a charge, and restores the potential of the charged body to that of surrounding objects.

To ascertain whether a flame of oxygen burning in hydrogen would similarly cause the hydrogen to assume the atomic state, a piece of apparatus was contrived in which such a flame burned in close proximity to a very thin iron plate, on the other side of which a Torricellian vacuum was maintained. No hydrogen passed through the plate: hence either the hydrogen was not atomically transferred, as oxygen is supposed to be under similar circumstances, or such atoms were unable to pass through the plate as they would have done if liberated electrically. It must be noticed, however, that it is conceivable that the double atom of hydrogen which we term a molecule may have united directly with the oxygen, without separating into its two components. The result of this experiment is therefore inconclusive.

It appears to me necessary to suppose that at a temperature far above that at which hydride of palladium is capable of existence, the palladium has still the power of so attracting the hydrogen that the molecule is split. This necessarily implies a gain of energy, so far as the splitting of the hydrogen molecule is concerned, for any energy lost by the temporary and transient union of hydrogen and palladium is at once gained during its escape on the other side of the partition. But the hydrogen in expanding, which it does on passing through the partition, loses energy, and hence, on the whole, energy will probably be lost during the process. It is to such theories, I think, that we must look to explain the passage of hydrogen through a palladium diaphragm.

(2) In answering the question why the pressure raised by the entering hydrogen is never equal to that of the atmosphere, I think it must be admitted that the gas contained in the palladium vessel is not without influence on the passage of the hydrogen. A diminution of the pressure of the external hydrogen by the addition of nitrogen considerably increases

the partial pressure of the internal hydrogen. Here the action of external nitrogen apparently neutralizes partially the effect of the internal nitrogen, and more hydrogen penetrates the metallic diaphragm. With gases other than nitrogen in the interior, the pressure of the hydrogen becomes more nearly equal to that on the exterior. The constancy of the results, however, proves that the deficiency is not due to experimental error.

This whole subject is full of difficulty. Experiments are in progress on the absorption of gases by platinum, and on the passage of gases through other metallic diaphragms, which may ultimately render an explanation possible. But I have thought it desirable to place these experiments on record, incomplete as they are, rather than wait for a complete solution to the problem.

I cannot conclude without acknowledging the able manner in which my late assistant, Mr. Percy Williams, has aided me in carrying out these experiments.

## DISCUSSION.

Mr. MOND thought the fact that rise of temperature accelerates diffusion tended to confirm Graham's view that the gases pass through openings in the solid, for increase of temperature would widen any pores which might exist in the metal.

The PRESIDENT enquired whether the author's argument against the possibility of palladium hydride condensing in the pores of the metal, because of its being unstable at the temperature employed, would be affected by the fact of water being capable of existing in contact with glass at temperatures much above boiling-point.

In reply Prof. RAMSAY said the President's suggestion might be true, but if so another condition must be fulfilled, viz., that the hydrogen molecules must be split up into the atomic or *nascent* state.

## XIX. *Experiments on the Relations of Pressure, Volume, and Temperature of Rarefied Gases.* *By* E. C. C. BALY, 1851 *Exhibition-Scholar in University College, London, and* WILLIAM RAMSAY, *Ph.D., F.R.S.*[*]

[Plate VII.]

THE experiments of which we give an account in the following pages are of two kinds:—first, they relate to the trustworthiness of measurements by means of the McLeod gauge; and second, they deal with the thermal expansion of gases at low pressures. The behaviour of the ingenious gauge invented by Professor Herbert McLeod has, so far as we know, not been carefully investigated. The thermal expansion of gases at low pressures has been the subject of two investigations, one by Mendeléeff, and one by G. Melander. But many researches have been made on the relations of volume to pressure at constant temperatures; and as there is an intimate connexion between the compressibility of gases and their thermal expansion, we think it desirable to give a short summary of the work which has already been done on the subject. It is obvious that if the product of pressure and volume of a gas diminishes with the degree of rarefaction, it is to be expected that its coefficient of expansion with rise of temperature will increase; whereas, if the $pv$ increases as observed by Mendeléeff and others, its coefficient of expansion will probably diminish.

### HISTORICAL RÉSUMÉ.

### 1. *Relation of Volume to Pressure at Constant Temperature.*

For more than twenty years the question of the validity of Boyle's Law, applied to rarefied gases, has been the subject of frequent articles in scientific journals. In 1873 Siljeström (*Bihang till K. Svenska Vet. Akad. Handlingar,* ii. p. 1) published in Swedish an account of experiments to test this important law. His method consisted in exhausting one of two stout cylindrical metal vessels connected together by means of a tube provided with an air-tight stopcock. Both vessels were placed in a large reservoir of melting ice in order to maintain temperature constant at 0°. Each vessel was provided with a mercury manometer; and while the larger of the two had no opening except the tube already mentioned, which connected it with the smaller vessel, the latter was joined by means of a brass tube with a stopcock to an ordinary exhausting air-pump, also furnished with a mercury gauge.

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[*] Read May 25, 1894.

The plan of operation was as follows :—The pressure of gas in the smaller vessel was reduced by means of the air-pump, communication with the larger vessel being cut off by means of the stopcock, and the pressure of the gas in both vessels was read on the mercury gauges attached to them, and also on that attached to the air-pump. The pressure registered by the gauge of the smaller vessel and by the air-pump gauge should of course be the same. Communication with the air-pump was then shut off. The stopcock between the two vessels was then opened, and gas passed from the larger to the smaller. After time had been allowed for equilibrium of temperature and pressure to be re-established, the pressures on the gauges were again read. The capacities of the vessels being accurately known, the product of pressure and volume could be calculated.

Sixteen series of experiments, each consisting of fourteen individual readings, were made with air; the diminution of pressure varied in these series from that of the atmosphere to 1·4 millim.; and by means of an accurate cathetometer the pressure was read to the second decimal place. The ratio of V (the volume of the closed reservoir) to V + V′ (that of both reservoirs) was calculated by means of the formula

$$E' = \frac{E(V + n\mu)}{V + V' + n'\mu} = \frac{eV'}{V + V' + n'\mu},$$

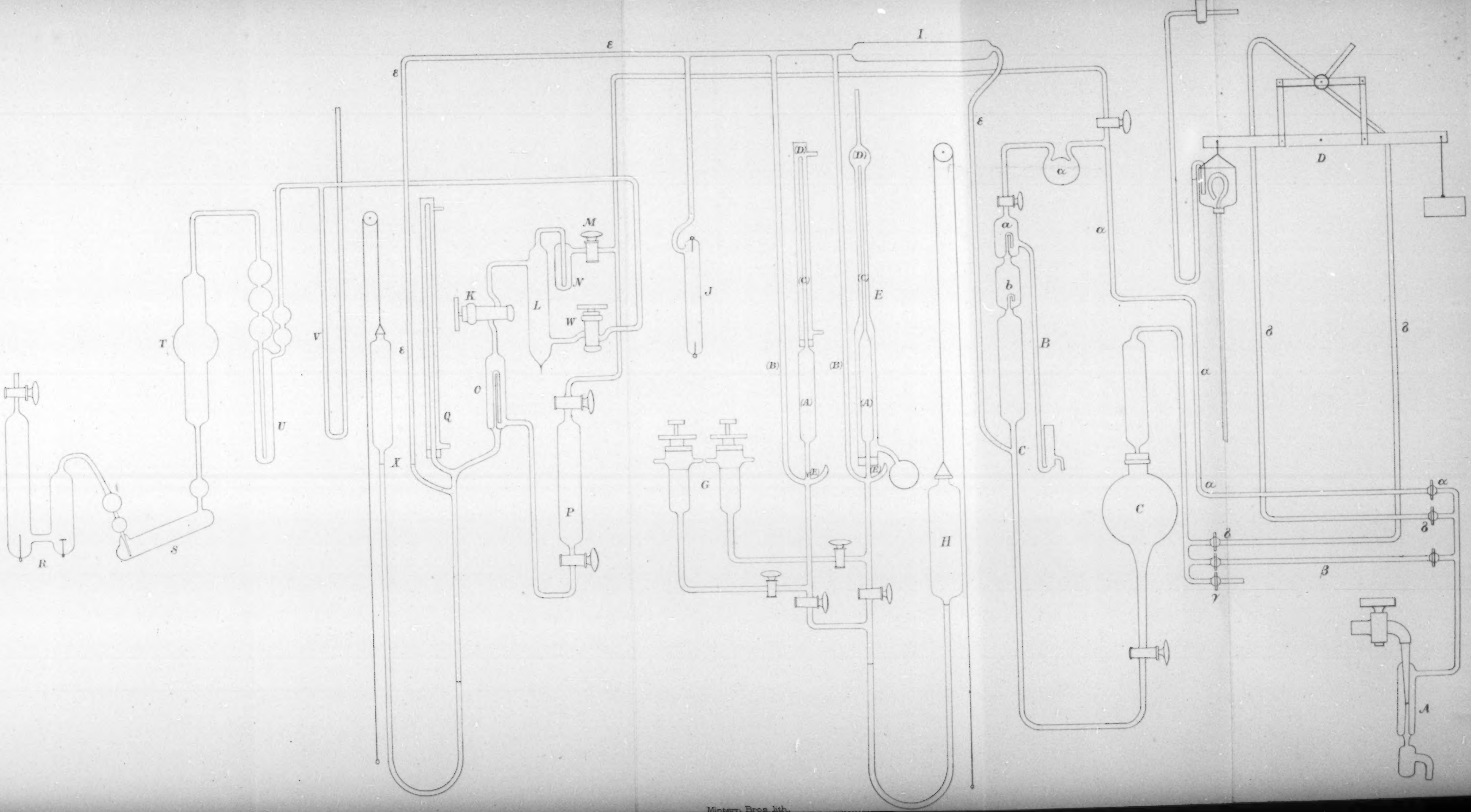
where

E is the original pressure of the gas ;

$e$, pressure read on gauge of second cylinder or of air-pump after exhausting ;

E′, pressure in cylinders after opening the stopcock ;

$n\mu$ and $n'\mu$, small corrections introduced, due to alteration



Mintern Bros. lith.

in total volume of apparatus owing to rise of mercury in the gauges. $n$ is a number of centimetres, $\mu$ the capacity of one centim. of the gauge.

$\beta$ (in following equation) $= \mu/\mathrm{V}$. Hence

$$\frac{\mathrm{V}'}{\mathrm{V}} = \frac{\mathrm{E}(1+n\beta)-\mathrm{E}(1+n'\beta)}{\mathrm{E}'-e}.$$

If the ratio $(\mathrm{V}+\mathrm{V}')/\mathrm{V}$ remains constant, Boyle's law holds; if, on the contrary, $(\mathrm{V}+\mathrm{V}')/\mathrm{V}$ be too great or too small, the pressure E′ would be either less or greater than corresponds with Boyle's law.

The results were averaged, series *a* and *b* being compared with series *c* and *d*; the latter with series *e* and *f*, and so on. This process yielded six sets of average values of $(\mathrm{V}+\mathrm{V}')/\mathrm{V}$ for air. The results follow :—

| Extremes of pressure. | V+V′/V. |
|---|---|
| 759 and 352 millim. . . | 1·47209 |
| 352 „ 164 „ . . | 1·47165 |
| 164 „ 77 „ . . | 1·46887 |
| 77 „ 37 „ . . | 1·46870 |
| 37 „ 18 „ . . | 1·46122 |
| 18 „ 7 „ . . | 1·46511 |

These values of V + V′/V decrease with falling pressure; the higher its value the lower the value of E′, and *vice versâ*. Assuming from Regnault's observations between 1 and 30 atmospheres that at a pressure of 1 atmosphere the value given above, 1·47209, is correct, and that Boyle's law holds under such a pressure, it follows that the *pv* of the air increases with decreased pressure. This conclusion, too, Siljeström considers to be rendered probable by Regnault's own work. For he, too, found that air is up to a certain degree more compressible at pressures higher than that of the atmosphere. For example, if Regnault's results for pressures between 3 and 6, between 6 and 12, and between 12 and 24 atmospheres be termed $k'$, $k''$, and $k'''$ respectively, then

$$k''/k' = 0{\cdot}997128\,; \quad k'''/k'' = 0{\cdot}999386.$$

The question of course is, Can these and similar ratios increase to above unity?

Siljeström found from similar but less numerous experiments with oxygen and with carbon dioxide that the variation in the ratio $(V+V')/V$ was in the same direction. His results with hydrogen are :—1·47247 at 759–351 millim.; 1·47302 at 351–162 millim.; 1·47258 at 162–75 millim.; and 1·46895 at 75–17 millim.

Siljeström's results are criticised by Mendeléeff and by Amagat. Any error which he might have made is cumulative, as pointed out by Van der Ven, whose work will be subsequently considered.

Mendeléeff's work is at present unfinished, or at least a description of it in full has not yet appeared. His main work appeared in Russian in 1875, and the first part consists of 267 pages folio; the second part is not yet published. We owe to the kindness of Dr. Jas. Walker an account of the contents of this large volume. Short accounts of Mendeléeff's general conclusions are to be found in French in the *Mélanges Physiques et Chimiques tirés du Bulletin de l'Académie Impériale des Sciences de St. Pétersbourg*, ix.; also *Annales de Chimie et Physique*, [3] ix. 1876. These abstracts leave much to be desired.

Mendeléeff states that he tried nearly a dozen different forms of apparatus before a satisfactory one was devised. This, he says, is figured in volume ii. table 15 (unpublished)*; but he gives the following description of it in a lecture delivered before the Imperial Russian Technical Society in January 1881. It consisted of an ovoid glass vessel, with a capacity of about 3½ litres, placed in a trough of water. The lower portion of this vessel terminated in a tube, one metre in length, provided at its lower end with a stopcock; the volume of air was determined by weighing the mercury run out from this vessel. A tube was sealed to this vertical tube, which served to fill the measuring-vessel with mercury when required. A capillary tube was attached to the upper part of the measuring-vessel; it communicated with two lateral descending tubes, through one of which gas could be introduced at will. It was closed by raising a reservoir of mercury, and covering an opening more than thirty inches below the top of the measuring-vessel; but when the reservoir was lowered, gas could be passed into the measuring-vessel, through the capillary tube. The second descending tube connected the measuring-vessel with a wide manometer, formed like a siphon; and by means of a reservoir it was possible to raise the mercury in the open limb to a mark with great accuracy. Corrections were introduced for temperature, measured by a differential air-thermometer, and also for the varying volume of the apparatus due to the different heights of the mercury in the manometer. It is easy to see how this apparatus could be employed to test Boyle's law. To test Gay-Lussac's, he describes the operation thus:—

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* Professor Mendeléeff informs us that a large part of the second volume is now in manuscript.

"The mercury is run out of the measuring-vessel to a mark on the capillary tube, and weighed. Let this be done at the temperature of boiling water. Now cool the bath to 0° by surrounding the vessel with ice—the pressure begins to diminish as is indicated by the manometer; but we will not allow it to do so. By means of the stopcock and the other capillary, we let mercury run into the vessel until the pressure of the gas at 0° becomes the same as it was at 100°. The apparatus is then raised to the ordinary temperature, and the mercury which entered the tube at 0° is run out and weighed. This weight and the previous one give us the data necessary for calculating the true coefficient of expansion of gases."

No final numbers are given in Mendeléeff's published papers, so far as we have been able to discover; but the general result is stated thus:—

The product of pressure into volume, $pv$, which according to Boyle's law should be constant, varies considerably with diminution of pressure; at low pressures $pv/dp$ is positive, *i. e.* the gas is less compressible than it would be if it followed Boyle's law. Stating the case broadly, it may be said that at low pressures gases approach the state of a liquid or a solid; or $pv$ increases with decrease of $p$; or $e/d$ increases, for $d = 1/v$.

We have thought it advisable to give a tolerably full description of Siljeström's and Mendeléeff's experiments, because they are described in languages not generally known; we may discuss the remaining researches on the subject in much shorter space, seeing that they are described in French and in German.

Amagat, in 1883 (*Annales de Chimie et Physique*, xxviii. p. 480), undertook experiments to test the results obtained by Siljeström and Mendeléeff, but was unable to confirm them. His conclusion is, that for the lowest pressures measured (6·54 millim.) the differences were sometimes positive, sometimes negative ; and that the necessary error of experiment was of an order of magnitude equal to that of the differences found. One of the main difficulties of observation was found in the diffraction of the walls of the manometer in which he measured the pressures to which the gases were exposed. He appears, however, to have been successful in overcoming this difficulty, by the use of polished plane surfaces ; but it is noteworthy that a suspicion of this source of error does not appear to have occurred to either of the former experimenters. Amagat also states that the utmost limit of measurement is probably overestimated at 0·01 millim. ; and indeed it is very difficult, if not impossible, to judge of the contact of two lines, the cross-wire of the cathetometer and the meniscus of the mercury in the gauge, to within such a minute distance. One of his criticisms of Mendeléeff's paper is worth quoting:—

"In M. Mendeléeff s experiments, a set of values of $pv$ are obtained corresponding to a tolerably limited range of pressures ; this would seem favourable to a knowledge of the direction in which these products alter ; but it is necessary to guard against possible illusion in this matter.

"A constant cause of error may affect all these products ; for as they deal with smaller and smaller values the effect will be more and more marked, and a regular variation may be conceived to exist, with no foundation in fact. Such an effect would be produced, for example, if the vacuum in the barometer were not absolute. It is certain, that whatever precautions be taken, this vacuum is not absolute ; the effect of this is to diminish the real value of the pressures, that is to say, too small pressures are read : hence the value of $p/p'$ is reduced, and since $p$ is smaller than $p'$, the values of $pv/p'v'$ are rendered too small ; and as the error increases with reduction of pressure, they will ultimately be less than unity."

Amagat proceeds to point out that even the vapour-pressure of mercury ceases to be negligible when a few hundredths of a millimetre cause the supposed deviation.

In 1886, C. Bohr (Wied. *Ann.* xxvii. p. 459) measured the pressures and volumes of rarefied oxygen. His conclusions are that at a temperature of $11^{\circ}\cdot4$ oxygen deviates from Boyle's law. For values of pressure greater than 0·7 millim., $(p+0\cdot109)v=k$; and for lower pressures, $(p+0\cdot070)v=k$. At 0·7 millim. therefore oxygen undergoes a sudden change and becomes more compressible. This is a very strange conclusion, but it has been confirmed by our work.

In criticising Bohr's work, it is to be noted that he employed very wide tubes, one as barometer, the other to contain the rarefied gas. His method of reading was ingenious. Finding it impossible to read the level of the mercury in such wide tubes with accuracy, he placed in each a glass ball, and read its upper surface. The readings therefore appear to be very accurate. But the shape of the meniscus of mercury is different in a nearly perfect vacuum and in a vessel containing gas; it is always flatter in the vacuous tube. Hence the volume read was probably always too small; and increasingly smaller as the gas was more compressed. This would render the value of the product $pv$ increasingly smaller, and necessitate the correction he applies. It would, however, not explain the breach of continuity which he observed.

Next in order of time comes a paper by F. Fuchs (Wied. *Ann.* xxxv. p. 430) in 1888. The lowest pressure which he measured was 248 millim.; but though he found deviations in the case of sulphur dioxide, hydrogen was normal.

In 1889, E. van der Ven carried out experiments by a method nearly identical with Siljeström's, but avoiding the possibility of cumulative errors which Siljeström's method involved. His conclusion is opposite to that of Mendeléeff and Siljeström; it is:—If a volume of air under low pressure, contained in a closed space, be doubled, it behaves as if its $pv$ decreased with decrease of pressure. Thus he finds

At 62 millim. pressure, $pv=0\cdot9873$,
At 31 „ „ $pv=0\cdot9811$,
At 16 „ „ $pv=0\cdot9740$.

Van der Ven used iron cylinders with walls 6 millim. thick, and it is unlikely that any appreciable alteration in their volume would be caused by the differences in pressure which occur in his experiments. He appears also to have been careful about the temperature of the vessels. But the latter part of his paper is occupied with a discussion of the capillarity of his mercury-gauge; and it appears to us that a possible source of error lies here. For the height of the meniscus of mercury in a gauge is undoubtedly altered by the pressure of the gas in contact with it; and as the gas was rarefied, the apparent difference in height of the mercury in a narrow gauge like the one he employed would be influenced not merely by capillarity, but also by the form of the meniscus. We regard it as probable that the capillarity of mercury, like that of other liquids, is altered by the gas in contact with it. In the empty, or comparatively empty part of the gauge, the capillary depression of the mercury is almost certainly not so great as in that limb exposed to gas; and the alteration of the pressure of the gas doubtless also alters the capillary depression. It would be worth while making this the subject of special experiments.

### 2. *Expansion of Gases at Constant Pressure, on Rise of Temperature.*

The last paper falling under our notice is one by G. Melander, published in 1892 (Wied. *Ann.* xlvii. p. 136). It deals with the thermal expansion of gases under reduced pressure. He concludes that the coefficient of expansion of air decreases from 0·003666 at 752 millim. to 0·0036594 at 232 millim., and again increases, with reduction of pressure, until at 6·6 millim. it amounts to 0·0037627; the turning-point of carbon dioxide is 76·2 millim.; with hydrogen there is no change in direction, but the coefficient increases from 0·0036504 at 764·5 millim. to 0·0037002 at 9·3 millim. These conclusions are opposed to those of Siljeström and Mendeléeff; for if the *pv* increases, as stated by these authors, it is to be expected that the coefficient of expansion should decrease with decrease of pressure.

Before concluding this historical sketch, we feel it necessary to point out that it is exceedingly unlikely that these experimenters were dealing with pure gases. It is true that their apparatus were filled with comparatively pure gases; but they do not seem to have realized the fact that on reduction of pressure, gas different from that with which they were dealing comes off the walls of the containing vessel. When this is of glass, a very considerable amount of carbon dioxide is always evolved. At high pressures, of course, this would make a small difference, probably inappreciable; but as the pressure becomes lower, a gas like hydrogen will be partly removed, and its place taken by carbonic anhydride. One can never be certain of the purity of the gas measured unless its vacuum-tube spectrum is free from that of other gases.

Another source of error, small in itself, but possibly important when the small deviations which the experimenters are endeavouring to measure are taken into consideration, is of the nature of that pointed out by Lord Rayleigh as applying to Regnault's determination of the comparative weights of hydrogen, oxygen, and nitrogen. It is that the volume of a glass (and presumably of an iron) vessel is considerably diminished if it be partially exhausted, owing to the external pressure of the atmosphere not being balanced by equal pressure in the interior. In Mendeléeff's experiments, for example, in which glass vessels were used, and in which the volume of the gas was ascertained by weighing the mercury run out of the vessel, it appears not unlikely that at low pressures the vessel contained less gas than at high pressures. The values of the products of pressure and volume, $pv$, might really remain constant with decrease of pressure; but as he read pressure directly, and assumed a volume which was probably too great, he registered an increase. We are informed, however, by Professor Mendeléeff, that he introduced a correction for this possible deviation.

All the researches described aim at a direct measurement of pressure. Now there is a limit to the possibility of such measurement, and when the pressure is low, the readings necessarily involve considerable relative error, the extent of which is difficult, if not impossible, to gauge.

We have therefore adopted a different plan, which admits of the observation of the behaviour of gas at pressures much lower than most of those previously employed. We have met with difficulties, subsequently to be alluded to, which may vitiate the results for some gases; but for hydrogen the results are fairly trustworthy.

To describe the method in a few lines:—Two McLeod gauges are exhausted in communication with each other: one is heated to a known high temperature; and at the same instant, both are closed; after cooling the pressure is read in both. The readings afford data from which the expansion of the gas may be calculated.

## DESCRIPTION OF THE APPARATUS.

The apparatus used for these experiments consisted essentially of two McLeod gauges placed side by side on a stand. These gauges were connected on the right to apparatus for exhausting them, and on the left to apparatus for admitting into them, when exhausted, measured quantities of the gas under examination.

The apparatus for exhausting shown on the right-hand side of the diagram (Pl. VII.) consisted of a water-pump A worked by high-pressure water, and capable of giving a vacuum of 11 millim. of mercury.

The exhaustion of the apparatus was commenced by this pump and completed by the mercury-pump B. This mercury-pump discharged the gas taken out at each stroke into a Torricellian vacuum which was sealed by two siphons *a* and *b*. By this means the gas in the large chamber of the pump suffered at most compression up to 4 millim. of mercury, so that the possibility of any considerable condensation of gas on the glass walls was eliminated, and each stroke of the pump removed as nearly as possible the theoretical quantity of gas.

For the preliminary exhaustion of the apparatus the water-pump A was connected with the top of the mercury-pump through the tubes and drying apparatus *αα*. When this preliminary exhaustion was complete, the mercury-pump was brought into action. The lowering and the raising of the mercury in the pump was brought about by alternately exhausting and filling with air the reservoir C which held the mercury. This could be done by hand: the exhausting by connecting it with the water-pump through the tube $\beta$, the admitting air by opening the tap $\gamma$; or, if preferred, by means of an automatic apparatus D through tubes $\delta\delta$. In this apparatus a three-way tap was turned through 90° by a lever, from one side of which was hung a cup fitted with a curved siphon and from the other a counterpoise, water being run into the cup through a flexible tube. The working of this apparatus was quite constant, and was accurately timed so that if it were left working for a known time the number of the strokes of the pump could easily be calculated. The mercury-reservoir C was placed at such a height that under atmospheric pressure the mercury would run over the top siphon *a*, care being taken that the distance from the siphon *a* to the T-piece *c* was considerably less than 30 inches. In the pump used it was 24 inches.

The mercury in the two McLeod gauges E and F was regulated for purposes of reading by coarse and fine adjustment-screws G; there was also a connexion with a movable mercury-reservoir H. The tube I contained pentoxide of phosphorus for drying purposes, and J was a vacuum-tube. This last was absolutely necessary, as it otherwise would have been utterly impossible to ascertain whether or not the apparatus was full of the gas under examination.

The gas to be examined was admitted through the tap K out of the chamber L. By means of the apparatus shown in the drawing any amount, large or small, of the gas could be admitted. The chamber L could be exhausted by the connexion through the tap M to the water-pump; a wash-bottle N containing mercury was interposed to prevent any diffusion backwards of air or water-vapour into the gas.

The amount of gas admitted was regulated by means of the siphon O which could be sealed by the mercury in the reservoir P. The mercury-level was adjusted by exhausting or filling with air the reservoir P in the same manner as with the reservoir C of the mercury-pump. The amount of gas admitted could, if desired, be measured in the gas volume-meter Q, which was designed on the model of the McLeod gauge. By means of this apparatus as small a quantity of gas as $\frac{1}{50,000}$ of a cubic centimetre could be accurately measured and admitted.

The two gauges E and F were placed close together on the stand in order to bring them as much as possible under the same conditions of temperature and exhaustion, and were almost exactly of the same size. They consisted of a large volume-chamber (A) about 90 cub. centim. in capacity, with a pressure-tube (B) at the side and volume-tubes (C) and (D) at the top. The tube (B) was about $\frac{1}{4}$ inch internal diameter; (C) consisted of a somewhat large capillary tubing, and (D) of a tube of very small bore. (C) and (D) were each about 250 millim. long. The volume and pressure tubes were accurately graduated in millimetres, the divisions on each exactly corresponding. The zero-points of the scales were placed at the top of (D) and at the corresponding place on (B). (B) was graduated 500 millim. below and 250 millim. above the zero-point. The total length of the volume-tube was of course 500 millim. A trap (E) was sealed below the chamber (A) in order to more accurately determine the volume of the gauge.

The calibration of the gauge was a most important point and was most carefully done. Every centimetre division on the volume-tube was taken as a reading-point, making fifty possible. At each of these points the capillary depression of the mercury had to be determined, *i. e.*, the difference in reading between the mercury levels in the pressure and volume tubes when both levels were under the same pressure. In order to measure these differences the extreme top of (D) was drawn out before a blowpipe to a fine point and the tip cut off. The gauge was then placed in an exactly similar position to that which it would occupy when finally fixed on the stand. Mercury was run in from the bottom and readings taken in the pressure-tube, with the mercury standing at each of the 50 reading-points on the volume-tube. After this had been done both with rising and falling mercury, the actual volumes corresponding to each of the 50 reading-points on the volume-tube measured from its upper end were determined. The tip of (D) was sealed, and accurately weighed quantities of mercury were run in from a fine capillary tube which was pushed up (C) and (D). From the numbers thus obtained the volumes represented by each reading-point could easily be calculated. Lastly, the total volume of the gauge from the top of (D) to the trap (E) was found by weighing the gauge empty and then filled with mercury. From the data thus obtained a table was constructed giving the capillary corrections and volumes in cubic centimetres for each of the fifty reading-points, due allowance being made for the meniscus. A column was also added of the values of R for each graduation, R being the ratio of the total volume of the gauge to the small volume at each point, or $\frac{V}{v}$. This ratio is used in calculating the vacuum in millimetres in the apparatus from a reading of the gauge. McLeod has shown that if a pressure $p$ be read, and R be the ratio at a point on the gauge, then the vacuum will be found from the expression $\frac{p}{R}$, or, if a second approximation be required, from

$$\frac{p+\frac{p}{R}}{R}.$$

The method of calculating the numbers read on the gauges was to multiply each pressure by each volume.

The following table shows the accuracy to be expected :—

| $v'$. | $c$. | $v''$. | $p'$. | $p$ in mm. | $v$ in c.c. | $pv$. |
|---|---|---|---|---|---|---|
| 120 | 7·2 | 127·2 | −11·0 | 116·2 | ·129 | 14·99 |
| 100 | 7·1 | 107·1 | +31·9 | 139·0 | ·107 | 14·93 |
| 80 | 7·1 | 87·1 | +86·9 | 174·0 | ·085 | 14·91 |
| 70 | 7·1 | 77·1 | +122·6 | 199·7 | ·074 | 14·94 |
| 60 | 7·1 | 67·1 | +166·5 | 233·6 | ·064 | 14·93 |

In the first column $v'$ are given the reading-points on the gauge volume-tube. In the second column $c$ are given the capillary corrections ; under $v''$ the result of applying these corrections ($v''=v'\pm c$). Under $p'$ the readings of pressure on the gauge, $p$ the actual pressure exerted by the mercury on the measured gas $p = v'' \pm p'$, plus or minus according to whether the reading of $p'$ is above or below the zero-point on the pressure-tube (B). Then follow the volumes represented by the reading-points $v'$, and lastly the product of pressure and volume. In addition to this, if the original pressure in the apparatus before reading the gauge is over ·1 millim. or thereabouts, this must be taken into account as the pressures found will be too small by this amount. The original pressure must therefore be found from the expression

$$\frac{p + \frac{p}{R}}{R}$$

as before shown and added to the values given in column headed $p$ above.

When the calibration of the gauges was finished they were ready for use. In fitting up the apparatus it was absolutely necessary to seal all joints with a hand blowpipe so as to prevent any possibility of leakage. The tap K for the admission of the gas to be experimented on was an exceptionally good one of oblique bore. It was lubricated with gummy phosphoric acid, and though in constant use for over a year never once showed the faintest trace of any leak whatsoever.

During the experiments the mercury of the gas volumemetre Q was kept at a known point $x$, so that the volume of the apparatus to be exhausted was from the point $x$ to the T-piece $c$ of the mercury-pump, the tubes $ee$, together with the two gauges and the vacuum-tube J. The gauges when read had their volume-tubes jacketed with cold water; and fitted on gauge E on the diagram is shown the jacket-tube used in the experiments at high temperatures.

Whilst working with these gauges we noticed the following points amongst others. First, when the gauge is not in use, the mercury should be kept as close as practicable to the trap, for if it be kept some way below, the gas between the mercury and the trap will, on raising the mercury, inevitably be driven into the gauge and considerably disturb the accuracy of reading, even as much as seven per cent. error having occurred from this cause.

Secondly, the 'sticktion' of the mercury in the capillary tubes of the gauges is very apt to introduce large errors into the results, especially at high vacua, when the pressures and volumes to be read are very small. To overcome this difficulty the tubes were continually tapped before reading, and many readings were taken both after ascent and descent of the mercury. That this was necessary may be shown by the fact that the before-mentioned capillary corrections when measured after ascent and descent of the mercury sometimes differed by as much as four millimetres.

It is also to be noted that the mercury must be raised very slowly, or gas will be trapped between the mercury and the glass. We also found it necessary to make the gauges of English lead-glass, as we found this to be the only glass that would stand the high temperature jackets without cracking.

## EXPERIMENTS TO TEST THE ACCURACY OF THE McLEOD GAUGE.

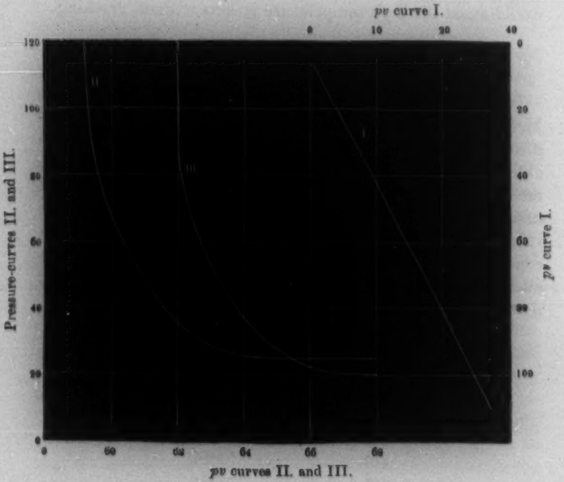
In order to determine once and for all the value of the McLeod gauge as a means of measuring vacua, some experiments were made with air. Many sets of readings were obtained, and they show the absolute failure of the gauge to measure vacua. It fails more and more as the vacuum improves. If the gauge had given trustworthy readings, the values of $pv$ obtained at all reading-points should have been constant. We give here a set of values of $pv$ measured at a moderate vacuum ($p$ here refers to pressure in the gauge; not to the vacuum in the apparatus) :—

| $p$. millim. | $pv$. |
|---|---|
| 4·1 | 100 |
| 4·1 | 81·83 |
| 4·1 | 69·921 |
| 4·3 | 67·25 |
| 4·6 | 59·57 |
| 4·6 | 41·78 |
| 4·9 | 33·47 |
| 5·0 | 23·09 |
| 6·3 | 15·09 |
| 8·0 | 9·427 |

The other sets of values of *pv* obtained during this exhaustion varied from 100–95, 100–74, 100–65, 100–38, 100–18, 100–14. In each of these sets the first and highest *pv* is raised to 100, and all other values in that set raised in proportion.

The set of values of *pv* given above, decreasing from 100 to 9 was plotted against pressures and the curve (No. I.) drawn which gives the value of *pv* constant for minimum pressure somewhere about 270. This gives a vacuum of 9 millionths of an atmosphere, instead of ·3 millionth.

But the curve, as thus drawn, is not correct, for the decrease in the values of *pv* is due to two causes. First, to the condensation of the gas on the glass as the pressure rises; and secondly, to the fact that Boyle's law does not hold good for air at such low pressures. In addition to this, the surface of glass is uneven and not of uniform porosity. Two sets of



readings of the two gauges at the same vacuum were obtained with carbon dioxide. These two series were calculated for the same volume and were plotted against pressures. The two curves crossed at a point (Nos. II. & III.). Now this point, pressure and volume being the same, should be a point of equal surface, but it is very far from being so. We see, therefore, that equal pressures may condense quite different volumes of gas on two equal surfaces of glass; or, in other words, that two equal surfaces of glass may have quite different capabilities of absorbing a gas at a given pressure, owing apparently to want of uniform porosity. A curve drawn for a set of readings is, therefore, not to be depended upon. Indeed, with some gauges, the readings are so erratic that it is exceedingly difficult to draw a curve at all, and one of the gauges made for these experiments had actually to be discarded for this very reason. Such results as these put beyond a doubt the total worthlessness of the gauge as a means of measuring low pressures with air or with carbon dioxide.

With hydrogen, however, the case is different. After the apparatus was absolutely filled with hydrogen, the sets of values of *pv* read on the gauges were constant, at least within the limits of experimental error.

We give a type of the series of readings we obtained :—

| *p.* millim. | *pv.* |
|---|---|
| 24·5 | 1·00 |
| 29·5 | 1·00 |
| 37·3 | 1·01 |
| 49·3 | 1·01 |
| 75·2 | 1·02 |
| 100·3 | 1·01 |
| 152·3 | 1·00 |

Many series of values of *pv* were obtained, and they prove that hydrogen expands quite normally between the limits 650 and 2·5 millim. of mercury pressure. We found it impossible with any accuracy to make readings in the gauges with a pressure smaller than 2·5 millim. These results also prove that hydrogen does not condense on a glass surface between these limits of pressure. By measuring the rate of exhaustion of an apparatus of known volume by a reservoir pump whose volume is also known, we found that hydrogen suffers no condensation on glass down to as low a pressure as ·000076 millim.

Let the volume of the apparatus be called V and the volume of the pump V′, then the pressure after a stroke of the pump will be $\frac{V}{V+V'}$ times the pressure which existed before the stroke. This value may also be found experimentally by dividing the pressure after a stroke of the pump by the previously existing pressure. We have called this ratio the Factor of Exhaustion. It is evident that the constancy of this factor of exhaustion depends not on the expansion of the gas but on the possibility of condensed gas coming off the walls of the apparatus, in which case its value would increase. We made many series of measurements to obtain the factors of exhaustion, and found that they were quite constant and equal to theory down to the extreme limit of exhaustion.

We give here the results tabulated.

In the column headed ratio of gauge readings are given the ratios of the readings of the two gauges obtained at each measurement. As these, of course, ought to be constant, they may be looked upon as a measure of the experimental inaccuracies of the work, and may be used to correct the deviations observable in the values of the factors of exhaustion. In the last column are given the values of $\frac{V}{V+V'}$ calculated from the apparatus and pump volumes. Any change in these indicates a new apparatus.

The last series vary a great deal owing to difficulties of reading, and also to the fact of the extremely high vacuum, pumping is performed by diffusion. The presence of mercury-vapour makes no difference in these experiments at all. When the mercury is raised in the gauges and the pressure on the gas rises, the mercury-vapour becomes condensed, and readings are only made of the hydrogen in the apparatus. When the

| No. of Stroke. | Vacuum. | Ratio of Gauge Readings $\frac{E}{F}$ | Factor of Exhaustion from gauge E. | Factor of Exhaustion from gauge F. | Theory. $\frac{V}{V+V'}$. |
|---|---|---|---|---|---|
| | | 1st Series *. | | | |
| Preliminary. | 4 millim. | 1·0359 | | | |
| I. ......... | 2·6 „ | 1·080 | ·5497 | ·5273 | ·550 |
| II. ......... | | 1·0555 | ·5431 | ·5512 | „ |
| III. ......... | | 1·0663 | ·5436 | ·5345 | „ |
| IV. ......... | | 1·0256 | ·5254 | ·5462 | „ |
| | | 2nd Series. | | | |
| Preliminary. | 4·9 millim. | 1·015 | | | |
| I. ......... | | 1·049 | ·5396 | ·5374 | ·540 |
| II. ......... | | 1·055 | ·5363 | ·5366 | „ |
| III. ......... | | 1·0476 | ·5376 | ·5414 | „ |
| IV. ......... | | 1·0475 | ·5430 | ·5432 | „ |
| V. ......... | | 1·0495 | ·5351 | ·5394 | „ |
| VI. ......... | ·11 millm. | 1·0444 | ·5463 | ·5515 | „ |
| | | Mean ... | ·5395 | ·5416 | |
| | | 3rd Series. | | | |
| Preliminary. | ·07 millim. | 1·040 | | | |
| I. ......... | ·0401 „ | 1·032 | ·5553 | ·5592 | ·557 |
| | | 4th Series. | | | |
| Preliminary. | Very high vacuum. | 1·0397 | | | |
| I. ......... | | 1·051 | ·6429 | ·6362 | ·560 |
| II. ......... | | 1·053 | ·5547 | ·5543 | „ |
| III. ......... | | 1·042 | ·6165 | ·6232 | „ |
| | | 5th Series. | | | |
| Preliminary | | 1·0521 | | | |
| I. ......... | | 1·0494 | ·5374 | ·5388 | ·548 |
| II. ......... | | 1·054 | ·5413 | ·5386 | „ |
| III. ......... | no connexion. | 1·058 | | | |
| IV. ......... | | 1·0626 | ·5346 | ·5325 | „ |
| V. ......... | | 1·060 | ·5389 | ·5401 | „ |
| VI. ......... | | 1·0427 | ·5401 | ·5493 | „ |
| VII. ......... | | 1·0368 | ·5395 | ·5426 | „ |
| VIII. ......... | | 1·0366 | ·5412 | ·5412 | „ |
| IX. ......... | | 1·0594 | ·5496 | ·5378 | „ |
| X. ......... | ·0068 millim. | 1·083 | ·6289 | ·6462 | „ |

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* In this series it had not been noticed that it was necessary to keep the mercury as close below the trap as possible, so as to avoid impelling gas into the gauge on raising the level of the mercury, in order to close it.

Table (*continued*).

| No. of Stroke. | Vacuum. | Ratio of Gauge Readings $\frac{E}{F}$ | Factor of Exhaustion from gauge E. | Factor of Exhaustion from gauge F. | Theory. $\frac{V}{V+V'}$. |
|---|---|---|---|---|---|
| 6th Series. | | | | | |
| Preliminary. | | 1·0549 | | | |
| I. ......... | | 1·0741 | ·5639 | ·5486 | ·548 |
| II. ......... | ·004 | 1·094 | ·5681 | ·5630 | " |
| III. ......... | ·0024 | 1·101 | ·6530 | ·6494 | " |
| 7th Series. | | | | | |
| I. ......... | Very high vacuum. | ...... | ·5875 | ·5583 | ·590 |
| II. ......... | | ...... | ·7362 | ·7670 | " |
| III. ......... | | ...... | 3857 | ·5912 | " |
| IV. ..... ... | | ...... | ·5634 | ·6012 | " |
| V. ......... | | ...... | ·6510 | ·5735 | " |

mercury is lowered again, mercury-vapour doubtless mixes with the hydrogen till a state of equilibrium is reached, the percentage of mercury-vapour depending on the pressure. In working the pump also the presence of mercury-vapour has no effect, for the pump-chamber when the mercury falls is empty of hydrogen, and if there is any hydrogen in the apparatus it will diffuse in through the mercury-vapour. This explains how it is possible to exhaust an apparatus filled with hydrogen so far that the pressure of the gas left is considerably below the pressure of mercury-vapour, though of course the actual pressure in the apparatus is not below that of mercury-vapour, for as fast as the hydrogen diffuses out of the apparatus into the pump, its place is taken by more mercury-vapour. Apparently, however, there is a limit to this, for we were not able to take out any more hydrogen than is represented by the last reading of the table above. The pressure of hydrogen in the apparatus was about ·000076 millim., while the vapour-pressure of mercury is about ·0002 millim.

An interesting calculation may be made with this value. If the gas under examination were air and not hydrogen, then a great quantity of air would have condensed on the glass when the mercury was raised in the gauge to take the reading. If the curve (No. I.) were applied to this value, we should obtain the reading of the vacuum ·0000022 millim. This curve, however, was obtained for air at greater pressure than the above, and the condensation would be still greater at ·000076 millim., so that this is probably the highest vacuum that has yet been measured.

These results prove that hydrogen does not in any way condense on to a glass surface on rise of pressure, and that therefore in working a McLeod gauge with hydrogen all the gas in the gauge is measured and none lost by surface-condensation. The McLeod gauge is accordingly trustworthy to a certain extent when working with absolutely pure hydrogen.

With carbon dioxide, however, the case is different. Several series of factors of exhaustion were obtained with this gas, and it was found that they steadily increase in value as the exhaustion proceeds. This is owing to condensed carbon dioxide coming off the walls of the apparatus. It seems even possible to reach to a pressure which is equal to the "vapour-pressure" of the carbon dioxide which is condensed on the walls. For in a particular experiment the factors of exhaustion increased steadily till they reached ·997, and 188 pumps more failed to make the slightest difference in the vacuum, as evidenced by the electric discharge in the vacuum-tube and by the gauge-readings. It would appear therefore that the pressure in the apparatus just equalled the pressure of the condensed carbon dioxide, and that as fast as the pressure was lowered by more pumping it was restored to its equilibrium by more carbon dioxide escaping from the pores of the containing walls. The vacuum was not very high, the *apparent* pressure being about one millionth of an atmosphere.

We found the converse of this when admitting measured volumes of carbon dioxide into a vacuum. In these experiments a gauge-reading was first taken and the *pv* calculated; then a known volume of carbon dioxide also calculated to *pv* was admitted. This last value multiplied by the ratio which the gauge volume bears to the rest of the apparatus will give the amount of carbon dioxide taken up by the gauge. This added to the previous value of *pv* read in the gauge ought to agree with the gauge-reading taken after the admission of the carbon dioxide. But we found that the measured *pv* was always smaller than that calculated. This shows therefore that some of the carbon dioxide condenses.

We give one series of measurements together with the values calculated from the known volume admitted:—

| Calculated. | Found. |
|---|---|
| 4·4 | 4·2 |
| 7·9 | 6·8 |
| 9·4 | 9·1 |
| 9·1 | 7·4 |
| 11·9 | 11·5 |
| 16·7 | 15·9 |
| 21·2 | 19·6 |

These results are a further proof that the McLeod gauge is of no value in determining the amount of rarefaction of carbon dioxide.

We also found it very easy to exhaust all hydrogen out of the apparatus if there were any condensed carbon dioxide on the containing walls. When the pump was started at about 10 millim. pressure, the spectrum of the gas in the vacuum-tube was only that of hydrogen. As the exhaustion proceeded the factor of exhaustion steadily increased while hydrogen slowly disappeared from the vacuum-tube and carbon dioxide became in evidence, till in a short time all the hydrogen had been pumped out and only carbon dioxide remained.

These facts may give an idea of the great difficulties we met with in filling the apparatus absolutely with hydrogen. This was a most lengthy and tedious operation. In spite of the fact that the apparatus used for the hydrogen experiments never had carbon dioxide put into it, the glass and the phosphorus pentoxide nevertheless contained great quantities of this gas condensed on them, the removal of which took a very long time. First of all the apparatus was exhausted as highly as possible and then the glass, especially the phosphorus-pentoxide tube, was raised to a high temperature with a Bunsen-burner, the exhaustion being kept very high in the meantime. Hydrogen was then admitted, and the apparatus again exhausted, the heating being still continued. This was repeated until no further carbon dioxide could be brought off the walls by the heating in the vacuum and until, after leaving it for a night, very highly exhausted, no spectrum of carbon dioxide was visible in the vacuum-tube when a current was passed. This process sometimes lasted a fortnight.

The foregoing results and the difficulties we met with in filling the apparatus with hydrogen emphasize our criticism on all previous work. For this fact of the condensation of carbon dioxide does not appear to have been noticed by previous experimenters. It would tend to make the read pressure too high, for carbon dioxide, being evolved from the glass with decrease of pressure, would mix with the gas under experiment and increase the apparent pressure. It is probably the reason why the product of pressure and volume has so often been found to increase with reduction of pressure.

To measure the expansion of hydrogen below the pressure of 2·5 millim. the thermal method was adopted. One of the two gauges was jacketed at a known temperature, and the expansion of the gas thus determined. Readings were taken on both the gauges, and the ratio of the two sets of values of *pv* obtained. When the mercury is lowered in the gauges the gas expands, and though its expansion below 2·5 millim. may be abnormal, this ratio of the values of *pv* remains the same. One of the gauges is then jacketed and the other read. This reading multiplied by the ratio before obtained gives the *pv* of the hot gas in the other gauge. The hot gauge is then shut off and allowed to cool, when it is read. The ratio of the readings of the gauge when hot and when cold is equal to the ratio of the absolute temperatures. To give an idea of the accuracy of the method we quote an example :—

*Preliminary Readings to obtain the Gauge Ratio.*

| Gauge E. | Gauge F. |
|---|---|
| *pv.* | *pv.* |
| 376·2 | 395·1 |
| 375·4 | 394·6 |
| 376·3 | 394·5 |
| 376·5 | 395·0 |
| 375·6 | 394·8 |
| Mean = 376·0 | Mean = 394·8 |

$$\text{Ratio}\,\frac{F}{E} = 1{\cdot}05.$$

Gauge F was then jacketed with aniline vapour. Barometer 764·9 at 0° C.

Readings after jacket.

| E. | F. |
|---|---|
| *pv.* | *pv.* |
| 379·84 | 247·60 |
| 379·71 | 247·41 |
| 380·11 | 247·94 |
| 379·78 | 248·25 |
| 379·17 | 247·71 |
| Mean = 379·71 | Mean = 247·782 |

Temperature = 12°·5 C.

When gauge F was hot the reading of gauge E was 379·71.

Therefore the reading of gauge F was

$$379{\cdot}71 \times 1{\cdot}05 = 396{\cdot}80.$$

Boiling-point of aniline at barometric pressure 764·9 millim. = 184°·66 C.

Therefore $396{\cdot}80 : 247{\cdot}782 :: x + 184{\cdot}66 : x + 12{\cdot}5$;

$\therefore \quad x = 273{\cdot}741.$

$\therefore$ Coefficient of expansion $= \frac{1}{273{\cdot}741}$.

Vacuum = 3·47 millim.

In making these experiments the readings were taken at the same reading-points throughout the whole operation so as to ensure accuracy. It will be evident that the volumes represented by the divisions on the gauge do not influence the result, and provided that the whole calculation is made from readings at the same points, the volumes at these points may be given any value whatever. The accuracy of the experiment therefore does not depend in any way on the accuracy of the volumes at the reading-points, but only of the pressures, which were very carefully read to within 0·1 millim.

The following coefficients of expansion of hydrogen were obtained :—

(T = temperature of jacket; $t$ = temperature of reading.)

| Pressure. | | T. | $t$. |
|---|---|---|---|
| 4·7 millim. | $\frac{1}{273\cdot5}$ | 184°·66 C. | 12°·5 C. |
| 3·47 " | $\frac{1}{273\cdot74}$ | 184·33 | 13·8 |
| ·25 " | $\frac{1}{276}$ | 132·32 | 14·7 |
| ·096 " | $\frac{1}{297}$ | 132·27 | 17·3 |
| ·077 " | $\frac{1}{300\cdot5}$ | 132·33 | 16·3 |

The purity of the hydrogen in these experiments was satisfactorily proved by both the constancy of the gauge-readings in each experiment and by the factor of exhaustion being equal to theory.

If the above results be plotted on a curve it shows that hydrogen expands quite normally till a pressure of ·4 millim. is reached, when its elasticity increases with further decrease of pressure. Many other experiments were made, with similar results.

Having thus satisfactorily proved that this method of determining the thermal expansion of hydrogen is capable of giving accurate results, we proceeded to apply it to determining the expansions of oxygen and nitrogen at reduced pressures.

In the case of oxygen the gas was made by heating permanganate of potassium, it was washed in caustic potash and dried by means of sulphuric acid and phosphorus pentoxide. Oxygen proved to be an exceptionally difficult gas to deal with, as it was found impossible to determine its purity by the electric discharge in the vacuum-tube, as the presence of dust or other combustible material led to the formation of carbon dioxide. This method therefore was of no use, and the purity of the oxygen was determined by the result obtained, as will be seen further on.

The coefficient of expansion of oxygen was found to be, from very careful experiments:—

5·1 millim. $\frac{1}{261}$,
5·3 " $\frac{1}{260}$,
4 " $\frac{1}{262}$.

These results are very fairly good, and being at such high pressures as 4 and 5 millim. may be said to demonstrate the absence of carbon dioxide, especially inasmuch as they give evidence of oxygen being too expansible, while carbon dioxide is the opposite. Each of these results, too, was obtained after a fresh filling of the apparatus, which in each case was most carefully done. Therefore the proof that they are measurements of the expansion of pure oxygen may be regarded as conclusive. As the results next obtained gave evidence that with decrease of pressure the coefficient of expansion still further increased, and as on the slightest sign of presence of carbon dioxide the apparatus was most carefully filled again with oxygen, there is no doubt that the expansion of pure oxygen was in each case measured. The presence of a small quantity of carbon dioxide would materially alter the results, as the value of the coefficient of expansion of this gas is so small at the pressures here dealt with.

The anomaly in the expansion of oxygen, first noticed by Bohr, was brought very strikingly under our notice in working with oxygen. The vacuum was at one time 1·4 millim., when, on a stroke of the pump being taken, the remaining gas, now at a pressure of about ·75 millim., behaved in a most extraordinary fashion. For example, the two gauges E and F, which are of the same volume within ·1 per cent., gave values of *pv* which, instead of being equal, had a ratio to one another of 1 to 8·8. We give the values :—

| Gauge E. | | | Gauge F. | | |
|---|---|---|---|---|---|
| *p*. | | *pv*. | *p*. | | *pv*. |
| 12·3 | = | 6·00 | 100 | = | 53·3 |
| 17·9 | = | 6·04 | 106·1 | = | 53·1 |
| 25·6 | = | 6·09 | 113·3 | = | 53·0 |
| 37·5 | = | 6·03 | 125 | = | 53·2 |
| | | 6·04 | | | 53·15 |

A large number of experiments were made, in which the gauges were continually opened and again closed and read, but the right ratio was not obtained until after 78 hours' rest. Then the readings in the gauge became normal, and an experiment was attempted to measure the coefficient of expansion, but the equilibrium of the gas was instantly disturbed, and the result came out about $\frac{1}{1500}$. When the apparatus was exhausted beyond this particular point, the behaviour of the gas became quite regular again, and two measurements of expansion were made. This same anomaly was met with again in subsequent experiments.

The coefficients of expansion of oxygen we obtained were as follows :—

| | | | T. ° | t. ° |
|---|---|---|---|---|
| 5·1 | millim. | $\frac{1}{261}$. | 132·11 | 11 |
| 5·3 | „ | $\frac{1}{260}$. | 132·0 | 11 |
| 4·0 | „ | $\frac{1}{262}$. | 131·6 | 13 |
| 2·5 | „ | $\frac{1}{251}$. | 132·1 | 9·4 |
| | | $\frac{1}{250·1}$. | 131·8 | 11·5 |
| 1·4 | „ | $\frac{1}{233}$. | 132·15 | 10·9 |
| ·083 | „ | $\frac{1}{244}$. | 131·71 | 9·1 |
| ·07 | „ | $\frac{1}{240·3}$. | 131·84 | 11 |

It will be seen, therefore, that the coefficient of expansion of oxygen decreases with decrease of pressure. Having a value of about $\frac{1}{261}$ at 5 millim., it increases steadily to where the change takes place. At a rarefaction greater than at this point, the value of the coefficient is again smaller, but it still appears to increase with further diminution of pressure.

It is difficult to account for the abnormal behaviour of oxygen as regards distribution in the gauges at a pressure of 0·75 millim. The only possible explanation appears to be that the temperatures of the two gauges must have differed to a small extent, and that the smallest difference in temperature produces quite an unusual disturbance in equilibrium.

Nitrogen was next experimented upon. The gas was prepared by absorbing the oxygen from air, first as far as possible by means of pyrogallate of potassium, and then by passing it over red-hot copper-gauze.

The experiments were carried out in the usual way, and there was no special difficulty connected with the filling of the apparatus with the gas.

The great difficulty in working with nitrogen was that experienced in obtaining satisfactory and concordant results in measurement of the ratio between the gauge-readings preliminary to the jacketing. This difficulty increased as the vacuum improved, and it was found impossible to obtain results of any value whatever at a less pressure than ·6 millim. The readings for the ratio were always taken with the utmost care, but in spite of this ratios sometimes differed amongst themselves as much as 2 per cent., which means a difference of 9 or more per cent. in the values of the coefficient of expansion.

The numbers obtained were as follows :—

| Pressure. | | T. | t. |
|---|---|---|---|
| 5·3 | $\frac{1}{304}$. | 132·55 | 8·8 |
| 4·97 | $\frac{1}{303·8}$. | 132·16 | 9 |
| 3 | $\frac{1}{301·6}$. | 132·42 | 8·5 |
| 1·1 | $\frac{1}{304}$. | 131·7 | 14 |
| ·8 | $\frac{1}{331}$. | 131·6 | 12·5 |
| ·6 | $\frac{1}{355}$.<br>$\frac{1}{343·5}$. | 132·1 | 11·5 |
| ·6 | $\frac{1}{377}$.<br>$\frac{1}{323}$. | 132·1 | 13 |
| ·6 | $\frac{1}{301}$.<br>$\frac{1}{327}$. | 131·6 | 13 |
| ·6 | $\frac{1}{371}$.<br>$\frac{1}{343}$. | 132·2 | 13 |

Mean of eight $\frac{1}{342·56}$ at ·6 millim.

These last values of the coefficient of expansion are in four sets, each set being the result of an entire fresh filling of the apparatus with nitrogen. The two values in each set have been calculated with the two extreme values of the gauge ratio that have been obtained during the experiments at this pressure ·6 millim. Though the results are not good, they nevertheless show that the coefficient of expansion of nitrogen for one degree Centigrade decreases with decrease of pressure.

To sum up the results :—(1) The coefficient of expansion of hydrogen with temperature decreases as pressure is lowered. It is normal down to a pressure of 0·1 millim. (2) The coefficient of expansion of oxygen is greater than the normal one, being 1/262 instead of 1/273 ; it increases with decrease of pressure to 1/233 at 1·4 millim. pressure ; at 0·7 millim. pressure it is erratic ; but at lower pressures it again becomes more constant, still showing, however, a tendency to increase as pressure is decreased. (3) With nitrogen the coefficient of expansion is lower than the normal (1/304) at pressures between 5 and 1 millim. ; at lower pressures, like that of hydrogen, its coefficient of expansion decreases ; that is the gas becomes more elastic. (4) So far as it was possible to experiment with carbon dioxide, its behaviour appears to resemble that of hydrogen and nitrogen ; but owing to the tendency which it has to condense and cling to the gauge, trustworthy measurements were impossible to attain. These results corroborate those of Mendeléeff and Siljeström, although they are deduced from thermal expansion, while theirs were deduced from the compressibility of the gas. And Bohr's results as regards the abnormality of oxygen were also confirmed, although likewise by a different method.

If it may be taken for granted, then, that the rate of expansion of gases decreases with decrease of pressure, it is necessary to inquire why this is the case. From the point of view of the kinetic theory, pressure is caused by impacts on the walls of the containing vessel of the molecules which it contains, due to their translational motion. The internal motion does not give rise to pressure. If, on communicating to a gas energy, by raising its temperature, it does not respond by a sufficient rise of pressure, it appears to us that the conclusion is inevitable that its internal energy is increased to a greater than usual extent compared with its translational energy. It is perhaps idle to speculate on the extreme final state of rarefaction ; but if this diminished rate of expansion were to continue to increase with tenuity, a point might conceivably be reached where all received energy would result in internal motion. Can this be the cause, or one cause, of phosphorescence in high vacua ?

In his *Allgemeine Chemie*, second edition, vol. ii. p. 32, Ostwald treats of the limiting phenomena of volume-energy.

He suggests that if it be conceivable that the volume of a gas is increased indefinitely, the volume-energy obtainable from a gas would also increase infinitely, involving the consequence that from a finite quantity of gas an infinite amount of heat of constant temperature could be converted into kinetic energy. He therefore suggests that at some very great, yet finite volume, the pressure should become zero, and the gas should therefore refuse to increase its volume. Instead of the expression for Boyle's law, $pv=c$, $(p+k)\,v=c$, where $k=\frac{c}{v_{\text{max}}}$, *i. e.* at a volume where $p=0$. Such a supposition would place an upper limit to the atmosphere. Similar considerations are also applied by him to gravitational energy.

The abnormal behaviour of oxygen is, if not more, at least equally difficult to explain. Some profound change must take place suddenly at the pressure 0·7 millim. Whether this change is of the nature of dissociation or not, cannot readily be determined; but the spectra of oxygen appear to show that it is able to exist in several modifications at low pressures.

The work described appears to us very incomplete; yet it has not been for want of time and trouble spent on it. The experiments are of extreme difficulty, and it has taken close on two years to arrive at the results chronicled, imperfect as they are. We are, however, somewhat cheered to learn that the experience of Professor Mendeléeff has in this respect been like ours—that a short column of figures can express the results of the labour of years.

University College, London,
20th May, 1894.

## Discussion (June 8, 1894).

Prof. Ramsay, in opening the discussion, recapitulated the chief points in the paper.

Siljeström in 1873 and Mendeléeff in 1875, he said, had both found that gases become less compressible than Boyle's law would give as rarefaction proceeds. Amagat in 1883 examined the subject, and concluded it was impossible to make measurements sufficiently accurate to decide the question one way or the other. In 1886 Bohr investigated the compressibility of oxygen, and found its behaviour abnormal at about 0·7 millim. pressure. Van der Ven's experiments (1889) led him to conclusions opposite to those of Siljeström and Mendeléef, and those of Melander (1892) gave support to Van der Ven's results. To decide the question at issue the authors took up the subject, and their results confirm the conclusions of Siljeström and Mendeléeff. They also prove that oxygen behaves abnormally at about 0·75 millim., as found by Bohr.

Prof. **Perry** said some of the terms used in the paper required alteration. The word "elasticity" was employed in several senses, sometimes being used to denote "*pv*," the product of pressure and volume, whilst at others its ordinary meaning was intended. He did not quite understand the connexion between *pv* and the thermal expansion to which the authors refer at the end of their paper. Taking Ostwald's equation for gases $(p+a)v=\mathrm{R}t$, he proceeded to show that the coefficient of expansion would be constant whether *pv* was constant or not.

Dr. **Burton** said he had been accustomed to think that as pressure was reduced gases approached the simple or "perfect" state. It was very desirable that similar experiments be made on other gases to ascertain if any had constant coefficients of expansion. He failed to see why the internal energy should increase as the pressure decreases, unless under these conditions energy travels more by radiation than by conduction or convection.

The **President**, speaking of the adhesion of gases to the surface of glass, suggested experiments on the effects produced by varying the ratio of the surface to the volume of the gas. On the subject of distribution of energy he was inclined to agree with Dr. Burton's view rather than with the authors' suggestion. One would not be led by *a priori* reasoning to expect that the internal energy would increase with decrease of pressure.

Prof. **Ramsay**, in reply, said that in the experiments on oxygen at about 0·75 millim. pressure the greater part of the gas was sometimes found in one McLeod gauge and sometimes in the other. Only after standing seventy-eight hours did the quantities trapped in the two gauges become equal.

The only explanation they could think of was that the temperatures of the gauges might not have been absolutely the same. Speaking of the suggested increase of internal energy with decrease of pressure, he said Prof. Dewar's experiments tend to show that there was little conduction through vacuous spaces.

The President thought Dr. Bottomley's researches had shown that radiation also falls off rapidly as the pressures become very small.

## XX. *The Clark Cell when Producing a Current. By* S. Skinner, *M.A., Lecturer at Clare College, and Demonstrator at the Cavendish Laboratory, Cambridge*[*].

### § 1. *Introduction.*

The electromotive force of the Clark cell when not producing any current has been frequently determined, and has been found to be of so constant a value that it is now used as a standard. These values of E.M.F. are for the cell when its poles are not united by a conductor. In the following an account is given of a series of experiments made on cells when producing currents, with the view of ascertaining, (1) how far the total electromotive force round the circuit differs from that of the open cell, and (2) how this new value for the E.M.F. changes when the current is maintained. If these quantities can be accurately measured, it follows that a cell might be used for producing currents of known value. Some experiments have been made on subject (2) by Threlfall and Pollock (Phil. Mag. November 1889), and their results are compared with mine in Sect. 8.

### § 2. *The Cells.*

The experiments were made on three cells, all much larger than the ordinary Board-of-Trade pattern of Clark cell.

Cell B, made July 1891, is the cell no. 90 described on p. 558 of the paper by Mr. Glazebrook and the author, Phil. Trans. 1892, A. The area of its exposed zinc surface is approximately 14·4 square centimetres.

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[*] Read June 22, 1894.

Cell L, made November 1892, is a much larger cell fitted up in a cylindrical jar 22 centim. high and 13 centim. in diameter. The zinc plate exposes an area of about 95 square centimetres.

Cell N, made July 1893, is intermediate in size and exposes about 29 square centimetres of zinc surface.

In all three cells the zinc plate, a piece of common zinc sheet, is placed horizontally, and they have the same E.M.F. within 2 parts in 5000.

## § 3. *The Effect of Uniting the Poles of a Cell.*

Let a cell of electromotive force E and internal resistance R have its poles joined by a wire of resistance $r$; then, providing R and $r$ are constant, and there is no polarization, the potential-difference between the poles will be $\frac{r\mathrm{E}}{\mathrm{R}+r}$. If, however, there is polarization, then this potential-difference will be $\frac{re}{\mathrm{R}+r}$, where $e$ is the value of the electromotive force required to produce the observed current.

The value of $-(\mathrm{E}-e)$ is the electromotive force of polarization.

In the large Clark cells described above E and $e$ are nearly equal when the current is not larger than ·01 ampere; this small difference is the subject of the following measurements. To obtain it, it is clearly necessary to find the value of the potential-difference $\frac{re}{\mathrm{R}+r}$, and of the resistances R and $r$. The measurements for R are contained in Sect. 4; $r$ consisted of thick wire coils or of a special wire resistance immersed in a large tank of paraffin oil; and the measurements of the potential-differences are contained in Sect. 6.

We shall now give an illustration, taken from an actual experiment, of what happens when the poles of a cell are united. On July 25th the cell L had an electromotive force, with its poles open, represented by 5009 on the compensator. The poles were then joined by a resistance of 1000 legal ohms, and their potential-difference, taken as quickly as possible, was then rather more than 4983 and rather less than 4984. Then a resistance of 500 legal ohms was substituted for the

1000; the potential-difference fell to 4959. Next, with 200 legal ohms the potential-difference was 4885. Lastly, the poles were opened, and the electromotive force of the cell was found to be 5009.

It is seen from these numbers that the cell recovered its electromotive force entirely after the various operations, and this is a typical instance of the behaviour of the cells. It should be mentioned here that these tests, as well as tests on two other cells, were made in the interval between the two sets of resistance observations recorded in the column of the table §4, headed "July 25th, Before—After."

## § 4. *Measurement of the Internal Resistance of the Cells.*

The important determination of the resistance of the cells was made by the method of Opposition, and by the use of an Alternating Current. By opposing any two of the cells, the resulting electromotive force was so small that, making them an arm in a Wheatstone's arrangement, there was no deflexion in the bridge-galvanometer. The bridge was fed with an alternating intermittent current by means of the commutator used by Mr. T. C. Fitzpatrick in his electrolytic measurements, B. A. Report, 1886, p. 328.

In this method the commutator is arranged to supply the currents in the galvanometer-circuit always in the same direction, so that an ordinary sensitive mirror-galvanometer can be used. The drum of the commutator has on each circular face eight insulated sectors of brass, those on one side being larger than those on the other. The larger sectors are connected by brushes to the battery-circuit, and the smaller to the galvanometer-circuit. They are arranged so that the battery connexion is always closed before that of the galvanometer, and is always broken after that of the galvanometer. A more complete description of the commutator, which works excellently, will be found in the paper already mentioned. Two or three Leclanché cells were used as the battery.

The method of connecting two cells together so as to have small resulting electromotive force is particularly applicable in the case of Clark cells, for they may be obtained of nearly equal electromotive force. In the case of the cells we are discussing, as mentioned in § 2, the greatest difference was never more than 2 in 5000.

The errors to which this method of measuring battery-resistance is liable are two : first, from self-induction, and second, from polarization at the electrodes. The only conductor containing self-induction of any magnitude is the galvanometer-coil, and as the method is a zero method this does not matter. The second error is eliminated by using an alternating current. However, following Fitzpatrick's method, tests were specially made for polarization by varying the ratio of the arms and by varying the speed of the commutator. For instance, on one occasion the resistance was between 11·0 and 11·1 with the usual speed for working; when the speed was more than doubled, the resistance retained the same value.

The three cells were measured in pairs, and the results in legal ohms are given in the following table, where C is the resistance of the connecting wires.

The words "Before," "After," refer to the relation of these measurements to those recorded in § 6.

| Cells. | July 20th. 16°·8. | July 23rd. 18°. | July 24th. 17°·8. | July 25th. 17°·8. | |
|---|---|---|---|---|---|
| | *After.* | *Before.* | | *Before.* | *After.* |
| N+B+C ...... | 13·20 | 12·8 | 13·1 | 13·25 | 13·11 |
| L+B+C ...... | 11·69 | 10·8 | 11·05 | 11·15 | 11·10 |
| N+L+C ...... | 11·04 | 10·7 | 10·9 | 10·98 | 10·90 |
| C ............... | 0·93 | 0·93 | | | |
| From which are calculated the following values of resistance :— | | | | | |
| L ............... | 4·30 | 3·88 | 3·96 | 3·97 | 3·98 |
| N ............... | 5·81 | 5·88 | 6·01 | 6·07 | 5·99 |
| B ............... | 6·46 | 5·99 | 6·16 | 6·25 | 6·19 |

The temperatures are those of the water-bath in which the cells stood ; the cells were not moved during the whole of the measurements. It will be noticed that the resistance of the cells is lower at high than at low temperature. This agrees with the fact that electrolytes decrease in resistance with increase of temperature.

### § 5. *The Resistances, and Apparatus for Comparison of Electromotive Forces.*

The compensating apparatus was the same as that described in § 8 of the paper by Mr. Glazebrook and the author already quoted. However, in the place of the Leclanché cells there described to produce the main current, I used one or two large Clark cells. The reason for this change arose from the irregular behaviour of the Leclanché cells when changes were made in the amount of current taken from them. The results of eleven series of observations were rendered useless on this account. When only one Clark was used in the main circuit, the standard cell for reference was a Helmholtz mercurous-chloride cell, § 7. When two Clark cells were used, the standard was some other Clark cell which was kept at rest.

The circuits, through which the currents from the cells under test were taken, consisted of thick wire coils from a legal ohm resistance-box for the values 1000, 500, 200 legal ohms, and of a german-silver wire of 147 legal ohms wound on an ebonite frame, which was placed in a tank of paraffin oil. This german-silver wire was always used when the current was maintained for any length of time, as from its construction its temperature could be very accurately observed.

### § 6. *Determination of the Electromotive Force of Polarization.*

By means of the method described in § 5 the results in the following table were obtained. The units of electromotive force are approximately $\frac{1{\cdot}4}{5000}$ volts.

| Cell and Date. | E.M.F. of cell open =E. | Potential-difference for the cell producing approximately :— | | | |
|---|---|---|---|---|---|
| | | ·0014 ampere $r=1000$ legal ohms. | ·0028 ampere $r=500$ legal ohms. | ·007 ampere $r=200$ legal ohms. | ·01 ampere $r=147$ legal ohms. |
| L. July 20... | 5010 | ...... | ...... | ...... | 4837 |
| L. „ 23... | 5009 | 4985 | 4961·5 | 4890·5 | |
| L. „ 25... | 5009 | 4983·5 | 4959 | 4885 | |
| N. „ 25... | 5007·5 | 4959·5 | 4912 | | |
| B. „ 25... | 5007 | 4971·5 | 4938·5 | 4841 | |

The simplest way to examine these results will be to calculate the electromotive force required to produce the observed current, when the cells are producing currents of different values. Using, then, the equation

$$e=\frac{\mathrm{R}+r}{r}\times \text{potential-difference},$$

with values of R from § 4 and of $r$ from § 5, we have the following values of $e$ :—

| | E. | $e$ for ·0014 ampere. | $e$ for ·0028 ampere. | $e$ for ·007 ampere. | $e$ for ·01 ampere. |
|---|---|---|---|---|---|
| L ...... | 5010 | ...... | ...... | ...... | 4981 |
| L ...... | 5009 | 5005 | 5001 | 4988 | |
| L ...... | 5009 | 5005 | 4999 | 4983 | |
| N ...... | 5007·5 | 4989 | 4971 | | |
| B ...... | 5007 | 5003 | 5000 | 4990 | |

From which we obtain the values for $\mathrm{E}-e$, the electromotive force of polarization being $-(\mathrm{E}-e)$.

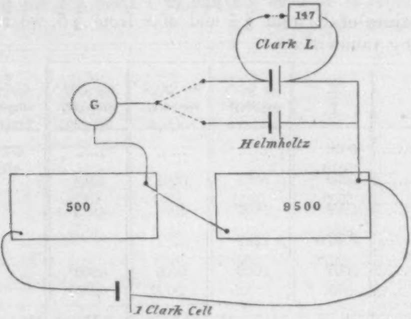
| | $\mathrm{E}-e$ for ·0014 ampere. | $\mathrm{E}-e$ for ·0028 ampere. | $\mathrm{E}-e$ for ·007 ampere. | $\mathrm{E}-e$ for ·01 ampere. |
|---|---|---|---|---|
| L ............ | ...... | ...... | ...... | 29 |
| L ............ | 4 | 8 | 21 | |
| L ............ | 4 | 10 | 26 | |
| N ............ | 18·5 | 36·5 | | |
| B ............ | 4 | 7 | 17 | |

It will be observed that for a given cell the electromotive force of polarization is directly proportional to the current-density.

### § 7. *Effect with Time, the Current being maintained.*

The experiments to be described in this section show how the potential-difference varies when the cell is allowed to produce a current for some time. For these experiments the standard of reference was a set of Helmholtz cells described in the paper quoted above, p. 618 ; they were immersed in a tank of paraffin oil. On January 17th they were submitted to a very rigorous test for constancy, extending over four hours, a Clark cell being the standard. It is not necessary to say anything further about them.

Fig. 1.



The arrangement used in the experiments is illustrated in the accompanying diagram (fig. 1), which clearly explains itself.

A single Clark cell was used in the main circuit for the reason that it is so much more steady than the usual two

| Time. | E.M.F. | Temperature. Oil. | Temperature. Water. |
|---|---|---|---|
| h m | | | |
| 11 14 | Helmholtz 6890+ | 13° | 12° |
| 12 15 | „ 6891− | 13 | 12·1 |
| 2 27 | „ 6891+ | 13·2 | 12·3 |
| 2 33 | Clark L through 147 l. ohms. | | |
| 2 36 | Clark L 9447+ | | |
| 2 37 | „ 9447+ | | |
| 2 38·5 | „ 9447+ | | |
| 2 49 | „ 9447 | | |
| 2 59 | „ 9446+ | | |
| 3 5·5 | „ 9446 | | |
| 3 13 | „ 9446− | | |
| 3 20 | „ 9445+ | | |
| 3 29 | „ 9445− | | 12·4 |
| 3 33 | Clark off | | |
| 3 35 | Helmholtz 6891+ | 13·3 | |
| 4 4 | „ 6891+ | 13·4 | 12·5 |

$$\text{Unit E.M.F.} = \frac{\text{E.M.F. Clark}}{10{,}000}.$$

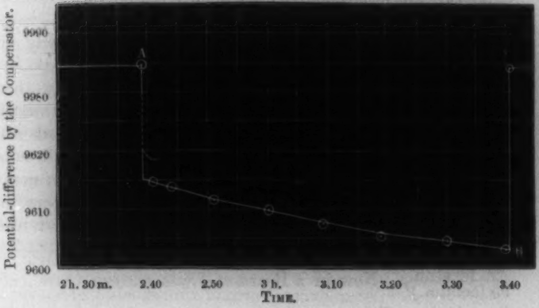
Leclanché cells, *vide* § 8. The complete results of a single experiment are given in the foregoing table.

Another set of observations is given in the accompanying diagram (fig. 2).

Fig. 2.

Jan. 16th, 1893. Temperature 12°.—At A, the Clark cell L was short-circuited by 147 ohms. At B, the circuit was broken.

Unit of E.M.F. $= \frac{\text{Clark}}{10{,}000}$



The four experiments made by this method gave an average fall of 7 units in the hour, and from the table § 6 we have the polarization on immediately making contact equal to 29 units $\left(\frac{\text{Clark}}{5000}\right)$, or 58 of our present units.

The polarization, or $-(E-e)$, for a current-density of $\frac{\cdot 01 \text{ ampere}}{100 \text{ centim.}^2}$ for cell L may at any time be expressed approximately by

$$-(58+7t),$$

where $t$ is the time in hours, and the unit of E.M.F. is $\frac{\text{Clark}}{10{,}000}$. Expressed in volts this is

$$-(\cdot 00834+\cdot 001\,t).$$

It is deduced from experiments on cell L, and only indicates the general order of magnitude of the effect with the other cells.

### § 8. *Conclusion.*

Throughout the calculations it has been assumed that the total electromotive force round the circuit is equal to that of the cell at rest; and therefore that the electromotive force overcoming polarization can be obtained by subtracting from the electromotive force of the cells at rest the observed current. With the exception of small Peltier effects, I know of nothing against this assumption.

The results of the experiments are :—

(*a*) The electromotive force of polarization varies directly with the current-density in a particular cell.

(*b*) The electromotive force of polarization slowly increases when the current is maintained.

From the magnitudes of the quantities found in these experiments, it follows that small currents of approximately known value can be obtained by the use of large Clark cells of small internal resistance, which may be neglected in comparison with the large external resistance. The experiments show that the large cell L when producing ·01 ampere was not at all disturbed. This corresponds to a current-density $\frac{\cdot 01 \text{ ampere}}{95 \text{ (centim.)}^2}$. Now in a Board-of-Trade pattern Clark cell there is generally an exposed area of zinc equal to 2 (centim.)$^2$, and as the current taken is never greater than $\frac{1\cdot 43}{10{,}000}$, a 10,000 ohm coil being used in series with it, it follows that the current-density with this value of current is very much below that which has been found to be safe in these experiments.

In the experiments of Threlfall the sign of the term depending on time was found to be negative. In some of my earlier experiments it appeared to be negative, but this was traced to irregularity in the working of the compensator ; and the effect has always been positive since the Clark cells have been used in the place of Leclanché, *vide* § 5.

## XXI. *A New Integrating Apparatus.* *By* A. SHARP, *B.Sc.**

(Abstract.)

THE paper describes an improved form of harmonic analyser, giving the amplitude and epoch of each constituent term, the mechanism of which is an inversion of that described in a communication made to the Society on April 13, 1894 (*ante*, p. 89). Numerous drawings accompany the paper, showing the various parts in detail. The mechanism is also shown to be applicable for integraphs, and by suitable modification may be employed for mechanically integrating differential equations of various forms.

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## XXII. *Magnetic Shielding by a Hollow Iron Cylinder. Simplest Case.* *By* JOHN PERRY, *F.R.S.**

I CONSIDER going and return electric conductors each at a distance $a$ from the axis in a diametral plane of the hollow cylinder, the current in each being C.

As to the inducing magnetic potential, all over one half of the cylindric surface of radius $a$ the potential is constant, $\pi C$, and all over the other half it is constant, being $-\pi C$. At a point P whose distance from the axis is $r$, the angle made by the axial plane through P and the plane through the conductors being $\theta$, it is evident that V, the inducing potential, is

$$V=4C\left(\frac{a}{r}\sin\theta+\frac{1}{3}\frac{a^3}{r^3}\sin 3\theta+\frac{1}{5}\frac{a^5}{r^5}\sin 5\theta+\&c.\right),$$

as this becomes $+\pi C$ or $-\pi C$ where $r=a$, and also satisfies $\nabla^2 V=0$.

Let the coefficient of $\sin n\theta$ in V be denoted by $Ar^{-n}$; let the corresponding coefficients be $A_1r^n+Ar^{-n}$ for the total (induced plus inducing) potential inside the tube; $A_2r^n+B_2r^{-n}$ total in the iron and $B_3r^{-n}$ in outside space. Let the inside and outside radii of the iron cylinder be $a_1$ and $a_2$. Then, on stating the equality of the potentials just inside and just outside the two surfaces, and also that the normal induction is the same on both sides, we have four equations, which enable the coefficients $A_1$, $A_2$, $B_2$, and $B_3$ to be calculated. The two important ones are

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* Read June 22, 1894.

$$B_3 = 4\mu A/\{(\mu+1)^2 - e(\mu-1)^2\},$$

where $e$ stands for ${a_1}^{2n}/{a_2}^{2n}$,

and $$A_1 = -A\rho(1-e)/{a_1}^{2n}(\rho^2-e),$$

where $\rho=(\mu+1)(\mu-1)$.

If we take $a_2=a_1+t$, and $t$ is small, since $\mu$ is large in iron, we have approximately

$$B_3 = A\bigg/\left(1+\tfrac{1}{2}\mu n\frac{t}{a_1}\right).$$

The higher terms are unimportant. Taking the first: the unshielded potential was $4Car^{-1}\sin\theta$, and it is converted by shielding into $4Ca\sin\theta/r\{1+\frac{1}{2}\mu t/a_1\}$.

Thus, taking $\mu=1200$, $a_1=150$ cm., $t=5$ cm., the first and most important term is reduced to the 1/21st part of its unshielded value. The other terms are reduced to 1/61st, 1/101st, 1/141st, &c., parts of their unshielded values.

In this case the potential inside is very little less than when there was no iron, $A_1$ being $-A/{a_1}^{2n}$ for all values of $t$ until $t$ is small; of course $A_1$ is 0 when $t$ is 0.

It is easy to extend the reasoning to several enveloping cylinders of iron, or to the case of any distribution of inducing potential which does not vary in a direction parallel to the axis.

## XXIII. *The Hatchet Planimeter.* *By* F. W. Hill*.

The hatchet planimeter consists essentially of a tracing-point and a convex chisel-edge rigidly connected, the point and the edge being in the same plane. When the point is moved along any line, the edge describes a curve of pursuit.

The object of this paper is to investigate how the instrument may be used to determine areas.

Let the tracer start from a point O inside the area, move along any line to the perimeter, then round the perimeter and back along the same line to O; the solution of the problem consists in finding an expression for the angle AOB between the initial and final positions OA, OB of the line joining the tracing-point and chisel-edge.

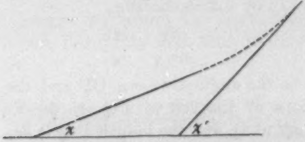
All attempts to express the area of the curve in terms of this angle proved futile except in a few special cases, such as the circle and square; but the magnitude of the angle may be found in the form of an infinite series, the most important term of which is a multiple of the area: The complexity of the result would seem to show that no simple geometrical explanation is possible.

Let the tracer move a distance $r$ along a straight line (fig. 1); then, if $\chi$, $\chi'$ be the initial and final inclinations of the rod to the line, $c$ the length of the rod, it is easily proved that

$$\tan\frac{\chi'}{2}=e^{\frac{r}{c}}\tan\frac{\chi}{2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Let the area of the curve be divided into infinitesimal triangles having their vertices at a point O inside the curve, and for their bases elements of the perimeter, the problem is

Fig. 1.



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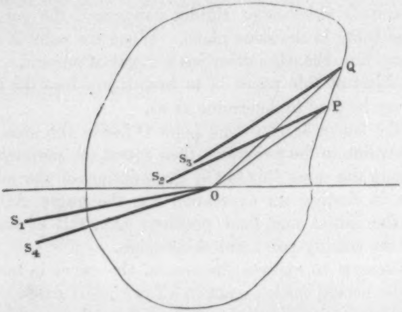
* Read June 22, 1894.

best attacked by making the tracer move round each of these triangles in turn, travelling along every radius-vector twice, in opposite directions. Taking any triangle OPQ (fig. 2),

Fig. 2.



let $\theta$, $\theta+d\theta$ be the inclinations of OP, OQ to a fixed line OX; $\phi$, $\phi'$, $\phi'+d\phi'$, $\phi+d\phi$, the inclinations of the rod to the fixed line in the positions $S_1O$, $S_2P$, $S_3Q$, $S_4O$ respectively; $r$, $r+dr$ the lengths of OP, OQ.

Then by (1)

$$\tan\frac{\theta-\phi'}{2}=e^{-\frac{r}{c}}\tan\frac{\theta-\phi}{2} \quad . \quad . \quad . \quad . \quad (2)$$

and
$$\tan\frac{\theta+d\theta-\phi'-d\phi'}{2}=e^{-\frac{r+dr}{c}}\tan\frac{\theta+d\theta-\phi-d\phi}{2}$$

for the motions from O to P, and from Q to O; hence

$$\frac{d\theta-d\phi'}{\sin(\theta-\phi')}=-\frac{dr}{c}+\frac{d\theta-d\phi}{\sin(\theta-\phi)}. \quad . \quad . \quad . \quad (3)$$

Also from (1) by differentiating,

$$\frac{d\chi}{\sin\chi}=\frac{dr}{c}.$$

Now if $\psi$ be the angle between OP and the tangent PQ, the inclinations of the rod to PQ are $\psi-\theta+\phi'$ at P, and $\psi-\theta+\phi'+d\phi'$ at Q, and the length P Q is $ds$;

therefore
$$\frac{d\phi'}{\sin(\psi-\theta+\phi')}=\frac{ds}{c},$$

or

$$\begin{aligned} cd\phi' &= \{\sin\psi\cos(\theta-\phi') - \cos\psi\sin(\theta-\phi')\}ds \\ &= rd\theta\cos(\theta-\phi') + dr\sin(\theta-\phi'). \end{aligned}$$

Substituting this value of $d\phi'$ in (3),

$$\frac{cd\theta - rd\theta\cos(\theta-\phi')}{\sin(\theta-\phi')} - dr = -dr + \frac{c(d\theta-d\phi)}{\sin(\theta-\phi)},$$

or

$$\begin{aligned} \frac{d\theta-d\phi}{\sin(\theta-\phi)} &= \frac{d\theta}{2}\left(1-\frac{r}{c}\right)\cot\frac{\theta-\phi'}{2} + \frac{d\theta}{2}\left(1+\frac{r}{c}\right)\tan\frac{\theta-\phi'}{2} \\ &= \frac{d\theta}{2}\left(1-\frac{r}{c}\right)e^{\frac{r}{c}}\cot\frac{\theta-\phi}{2} + \frac{d\theta}{2}\left(1+\frac{r}{c}\right)e^{-\frac{r}{c}}\tan\frac{\theta-\phi}{2} \end{aligned}$$

by (2);

$$\begin{aligned} \therefore\ d\theta-d\phi &= \left[\left(1-\frac{r}{c}\right)e^{\frac{r}{c}}\cos^2\frac{\theta-\phi}{2} + \left(1+\frac{r}{c}\right)e^{-\frac{r}{c}}\sin^2\frac{\theta-\phi}{2}\right]d\theta \\ &= \tfrac{1}{2}\left[\left(1-\frac{r}{c}\right)e^{\frac{r}{c}} + \left(1+\frac{r}{c}\right)e^{-\frac{r}{c}}\right]d\theta \\ &\quad -\tfrac{1}{2}\left[\left(1+\frac{r}{c}\right)e^{-\frac{r}{c}} - \left(1-\frac{r}{c}\right)e^{\frac{r}{c}}\right]d\theta\cos(\theta-\phi) \\ &= \left(1-\frac{r^2}{2c^2}-\frac{r^4}{8c^4}-\frac{r^6}{144c^6}-\ldots\right)d\theta \\ &\quad -\left(\frac{r^3}{3c^3}+\frac{r^5}{30c^5}+\ldots\right)\cos(\theta-\phi)d\theta. \end{aligned}$$

Or

$$\begin{aligned} c^2d\phi &= \frac{r^2d\theta}{2} + \frac{r^4}{8c^2}d\theta + \frac{r^6}{144c^4}d\theta \\ &\quad + \left(\frac{r^3}{3c}+\frac{r^5}{30c^3}+\ldots\right)d\theta\cos(\theta-\phi). \quad . \quad . \quad (4) \end{aligned}$$

This equation gives the change in the direction of the rod when the tracing-point has moved round an elementary triangle and integrating round the curve there results, for the angle between the initial and final positions of the rod, the expression

$$\begin{aligned} c^2\Phi &= \mathrm{A} + \frac{1}{8c^2}\int r^4d\theta + \frac{1}{144c^4}\int r^6d\theta + \ .\ . \\ &\quad + \int\left(\frac{r^3}{3c}+\frac{r^5}{30c^3}+\ .\ .\right)\cos(\theta-\phi)d\theta \end{aligned}$$

where A is the area of the curve, and the integrations extend from $\theta=0$ to $\theta=2\pi$. Thus if the greatest breadth of the curve is less than the length of the planimeter, the most important term in the expression is A, and it remains to estimate the effect of the other terms.

First, considering those terms which depend only on the position of O,

$$\frac{1}{8c^2}\int r^4 d\theta=\frac{Ak^2}{2c^2},$$

where $Ak^2$ is the moment of inertia of the area about the polar axis through O. This term is therefore least when O is the mass-centre of the area.

$$\frac{1}{144c^4}\int r^6 d\theta \text{ is less than } \frac{2A}{144}\left(\frac{a}{c}\right)^4,$$

where $a$ is the greatest radius-vector from O, and, if $\frac{a}{c}$ is as great as $\frac{1}{8}$, is less than one per cent. of the area.

Of the terms depending on $\phi$ the most important is

$$\frac{1}{3c}\int r^3 \cos(\theta-\phi)d\theta.$$

In these small terms the value of $c^2\phi$ at any point may be taken to be the area of that part of the curve already described by the tracing-point, and the terms can be evaluated when the equation of the curve is known. If, however, the area of the curve is less than that of a square of side $c$, so that the greatest value of $\phi$ is less than 1, it is easy to approximate.

$$\frac{1}{3c}\int r^3 \cos(\theta-\phi)d\phi=\frac{1}{3c}\int r^3\cos\theta d\theta+\frac{1}{3c}\int r^3\phi\sin\theta d\theta$$
$$-\frac{1}{6c}\int r^3\phi^2\cos\theta d\theta+\ldots$$

Now, the axis of $x$ being the initial position of the rod,

$$\frac{1}{3c}\int r^3\cos\theta d\theta=\frac{1}{c}\int x dA=\frac{A\bar{x}}{c},$$

where $\bar{x}$ is the abscissa of the mass-centre of the area. The other terms are multiplied by $\left(\frac{a}{c}\right)^3$, and being integrals of oscillating quantities are very small.

Thus

$$c^2\Phi = A + \frac{Ak^2}{2c^2} + \frac{A\bar{x}}{c} + \frac{P}{c^3},$$

where P is very small.

If O is the mass-centre of the curve $k^2$ is a minimum and $\bar{x}=0$. In this case

$$c^2\Phi = A\left(1 + \frac{\rho^2}{2c^2}\right)$$

very nearly, where $A\rho^2$ is the moment of inertia about the polar axis at the mass-centre.

If O is not near the mass-centre, let the tracing-point be moved again round the perimeter, following the same path as before, but with the initial direction of the instrument exactly reversed; the effect of this is to change the sign of $c$ and to give

$$c^2\Phi' = A + \frac{Ak^2}{2c^2} - \frac{A\bar{x}}{c} - \frac{P}{c^3};$$

hence

$$\frac{c^2}{2}(\Phi + \Phi') = A + \frac{Ak}{2c^2}$$

$c\Phi$ being the distance between two indentations may perhaps be measured to within $\frac{1}{100}$ inch, so that there will be an error in $c^2\Phi$ of at least $\frac{1}{20}$ sq. inch, if $c$ is 10 inches; if, therefore, $\frac{Ak^2}{2c^2}$ is less than $\frac{1}{20}$ sq. inch, it may be neglected.

Of curves with the same greatest breadth, the circle has the greatest area, and $\frac{Ak^2}{2c^2}$ is less than $\frac{1}{20}$ sq. inch for a circle of radius $1\frac{1}{2}$ inches.

Finally, then, if O be near the mass-centre, and the greatest breadth be less than 3 inches, the formula $c^2\Phi = A$ will give a result as accurate as the nature of the instrument will allow; for greater areas the value of $\frac{Ak^2}{2c^2}$ must be estimated and taken into account. Also it is easily verified that if $\Phi$ is less than $\frac{3}{13}$, or the area less than 23 sq. inches, it is sufficient to measure the chord of the arc $c\Phi$ instead of the arc.

### Discussion.

Prof. **Henrici** did not agree with the statement that the instrument was necessarily inaccurate, and thought geometry might aid analysis to find the proper starting point. For a symmetrical curve he had shown that a point existed, starting from which the area traced by the hatchet end was zero.

Dr. **Macfarlane Gray** thought Prof. Henrici's latter argument was vitiated by his figures not being correctly drawn; but this Prof. Henrici disputed.

Mr. O. G. **Jones** said Prof. Henrici's construction was not obvious, for the cusp curves traced by the hatchet end depended on the starting point.

Mr. **Yule** suggested that by shortening the planimeter it might be possible to bring the third and second terms of Mr. Hill's formula into greater prominence, and by going round the curve more than once determine the first and second moments.

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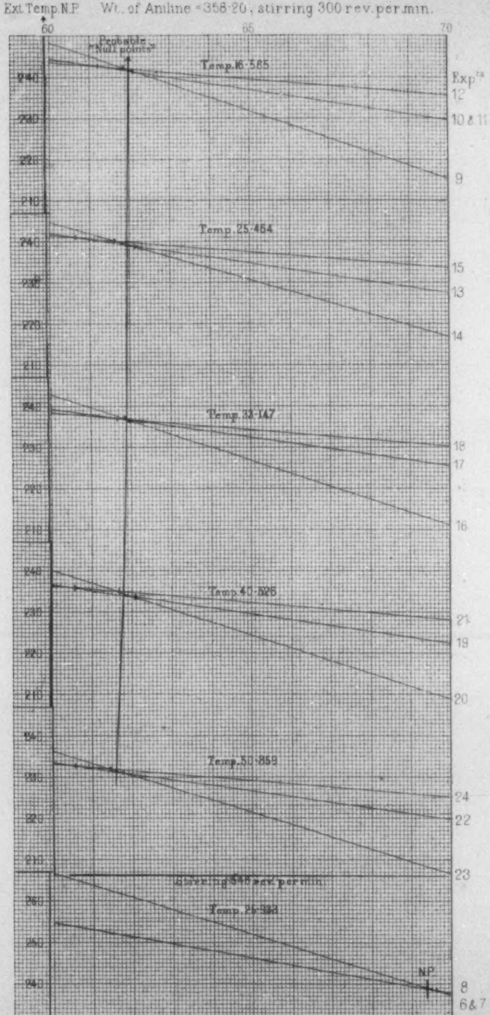
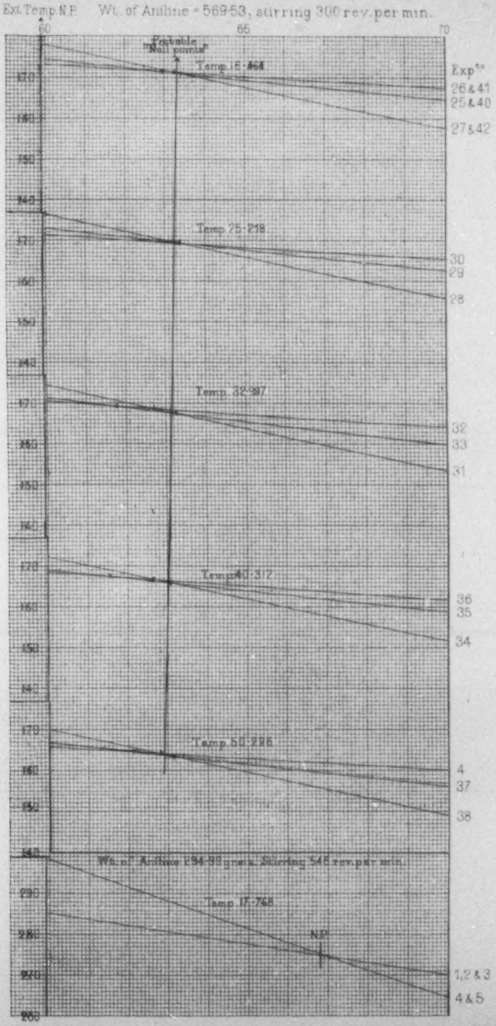
## XXIV. *The Influence of Temperature on the Specific Heat of Aniline.* *By* E. H. Griffiths, *M.A.*[*]

[Plates VIII. & IX.]

Our knowledge of the effect of changes of temperature upon the specific heat of substances is limited. The reason of this is evident, for, in addition to the difficulties of thermometry, the experimental methods usually adopted are based on comparisons in which water is used as a standard, and our knowledge of its capacity for heat at different temperatures is far from satisfactory. The conclusions of Rowland (1879), of Bartoli and Stracciati (1893), and my own investigation completed in 1892, all point to the fact that the specific heat of water diminishes as the temperature rises to 20° C., at which temperature Bartoli and Stracciati find it is a minimum. My observations did not extend beyond 27° C., up to which temperature I found no signs of a minimum,

[*] Read October 26, 1894.


Ext. Temp. N.P.
Wt. of Aniline = 358·20, stirring 300 rev. per min.
60
65
70
Probable "Null points"
Temp. 16·565
Expts
12
10 & 11
9
240
230
220
210
Temp. 25·464
15
13
14
Temp. 33·147
18
17
16
Temp. 40·526
21
19
20
Temp. 50·859
24
22
23
Stirring 546 rev. per min.
Temp. 25·332
260
250
240
230
N.P.
8
6 & 7



Edwin Wilson Cambridge.

which Rowland places at about 34° C. When such discrepancies exist with regard to the standard, it is not surprising that the conclusions arrived at regarding other substances are unsatisfactory.

For other reasons water is by no means an ideal standard for calorimetry. Its capacity for heat is so great that the changes in temperature caused by the immersion in it of bodies whose specific heats are small are too minute to be measured with exactness under ordinary circumstances. The difficulty is surmounted in practice by causing the immersed body to cool through a considerable range. Other errors are, however, introduced by this method, for the transference of the hot body into the cool water can rarely be conducted without loss of heat. What we require is a liquid of small capacity for heat whose temperature-coefficient of specific heat is accurately known. It should also, if possible, be a liquid easily obtainable in a fairly pure state and should have a low vapour-pressure at ordinary temperatures. I believe that in Aniline we possess such a liquid, and I hope to be able to adduce sufficient evidence to lead to the conclusion that its specific heat is now known with considerable accuracy over a range of 15° to 52° C.

The method I have adopted is an old one, viz. a supply of heat to the interior of the calorimeter by means of an immersed conductor whose ends are kept at a constant potential-difference. I admit that there are difficulties inseparable from the method (such as doubts as to the actual resistance of the conductor when its temperature is raised by the current, &c.), but when once these difficulties are overcome, there is no such accurate means of determining the quantity of heat passed into a calorimeter in a given time.

The limits of this paper forbid any detailed account of the somewhat complicated apparatus used in this investigation, and I do not contend that it is of the form which I should have selected had my object simply been to determine the specific heat of aniline. I am at present engaged in a determination of the latent heat of evaporation of water and other liquids at different temperatures, consequently the apparatus has been designed and put together in anticipation only of that investigation, and many portions of it are unnecessary and in fact detrimental to the inquiry I am now describing. Hence I have been compelled to adopt methods of observation which may not, at first sight, seem the most advantageous.

I have in my possession an apparatus for maintaining the walls of a chamber at a constant temperature. The arrangement has been fully described in a communication entitled "The Mechanical Equivalent of Heat," Phil. Trans. clxxxiv. A (1893), and as I shall somewhat frequently have to refer to this paper, I will now label it with the letter "J." Briefly, the apparatus as there described consists of a tank containing about 20 gallons of water within which is a steel chamber shaped somewhat like a hat-box with vertical sides, the space between the double walls and floor containing rather more than 70 lbs. of mercury, which communicates by a narrow tube with a gas-regulator differing but little from the ordinary pattern. Thus a row of about 50 tiny gas-jets (placed under a tube through which water is always flowing) are so controlled as to be distinctly affected by a change of $\frac{1}{400}$° C. in the temperature of the steel chamber. An addition has been made to the apparatus since the publication of the description in paper J, where it is stated that tap-water continually passed into the tank through a silver tube placed above the gas-jets: this plan answered admirably from the temperature of the tap-water (10° to 12° C.) to about 30° C. Last year, however, Prof. Callendar and I wished to use the tank for purposes of comparison of platinum and air thermometers up to 50° or 60° C., when it was found that alterations in temperature presented themselves, occasionally amounting to as much as $\frac{1}{50}$° C.,—the lag in the temperature of the large mass of mercury being so great that when the gas was lowered by the action of the regulator, the resulting inflow of cold water tended to lower the temperature of the tank before the reaction of the regulator could again heat the inflow. As now arranged, when working above temperatures about 20° C. a small motor acts as a heart and, the tap-water being shut off, pumps the tank-water itself round through the silver tube placed above the gas-jets. The water, by passing through the pump &c., is slightly cooled: thus the work of the regulator is confined to simply supplying the heat lost by convection, radiation, &c., and it performs this task admirably. As an illustration, I may mention that in the series of over 50 experiments treated of in this communication on only one occasion did the temperature of the steel chamber change by as much as $\frac{1}{100}$° C. throughout the duration of an experiment. On the solitary occasion that a change amounting to nearly $\frac{1}{50}$° C. was observed, the cause was found in the caking of the lime through which the gas was passed on its way to the regulator, and, in consequence, the experiment was discarded before working out its results.

A large screw, placed in the tank-water, revolved at about 800 times per minute and raised a considerable sea—the flow passing round, under, and over the steel chamber, the top of which was about 4 in. beneath the surface of the water.

The calorimeter was formed of brass and was suspended by glass tubes which, after passing through the lid of the steel chamber and through the water, projected above the lid of the tank. The diameter and depth were each about 10 centims. and the capacity about 700 cubic centims. Within it was suspended a silver flask with which three silver tubes communicated. One was connected with a glass tube passing to the exterior through which substances could be introduced. The second tube, which was about 18 feet in length, was, after leaving the top of the flask, twisted into a spiral within the calorimeter ; the other end, terminating in the lid of the calorimeter, was then connected by a glass tube with a four-way tap entirely immersed in the outer tank. The third tube, which opened into the bottom of the flask, communicated with about 30 feet of copper tubing placed in the tank-water. The object of the whole arrangement was that the gas on leaving the calorimeter (after evaporating any liquid in the flask) should have acquired the temperature of the calorimeter, and that any gas passed into the flask should assume the temperature of the outer tank. True, this portion of the apparatus was not necessary to the experiments on aniline, but I have felt it advisable to describe it, as explaining some of the subsequent operations.

A coil of fine german-silver wire, supported on glass pillars, was placed within the calorimeter and so arranged as to surround the silver flask. Communicating with this coil were four leads—Nos. 1 and 2 of which were fastened to one end, and Nos. 3 and 4 to the other end of the coil at the roof of the calorimeter, and, passing up through the steel vessel, communicated with the exterior. Nos. 1 and 3 formed the ends of a circuit in which were placed a high-resistance galvanometer and the Clark cells ; Nos. 2 and 4 a circuit which contained a rheochord of special construction (for a description see paper J), reversing-keys, and storage-cells. It was thus possible to maintain the ends of the calorimeter-coil at a difference of potential equal to that of any number of Clark cells ; and I am convinced that the variations in the potential-difference during the course of an experiment rarely amounted to $\frac{E}{10,000}$. (The grounds on which this somewhat bold statement is based are fully given in paper J, p. 283.) The contents of the calorimeter could thus be heated or cooled without any disturbing effects from external causes. By means of the electrical arrangements above described, the supply of heat could be regulated at will and accurately determined, while, by the insertion into the flask of a volatile liquid such as ether, it was possible, by adjusting the current of dried air, to regulate the rate of cooling.

Particulars of the Clark cells have already been published (paper J, pp. 286–288), and the whole 36 maintain to-day almost exactly the same relative values as they had when compared with the Cavendish standard in 1892 : there is, therefore, every reason to believe that their absolute value remains unchanged. I have not yet had time to repeat the comparison with the Cavendish standard, but I hope to do so shortly. I do not, however, anticipate that any correction will be found necessary. The whole of these cells were contained in a bath, through which the tap-water was turned by means of a regulator whenever the temperature exceeded 15° C.

The calorimeter previously described differed considerably from that used in my determinations of the mechanical equivalent. During these experiments the air-pressure in the space between the walls of the calorimeter and those of the steel chamber containing it was reduced to from ·5 to ·2 millim. as measured by McLeod's gauge; and my observations proved that there was a strangely rapid diminution in the loss by convection, &c., when the pressure fell below half a millimetre*. I proposed, however, during the experiments for which this second calorimeter was designed to maintain the calorimeter and the steel chamber at nearly equal temperatures, and it did not, therefore, appear so necessary to guard against convection and radiation gains and losses. Previous experience had convinced me of the absolute necessity for keeping this intramural space dry, for I found that the slightest moisture in the contained air has the most astonishing effect in changing the conditions. It was therefore necessary that all joins should be absolutely tight, for the lid of the steel chamber was under water, and I proposed, in the preliminary experiments, to place water within the calorimeter. The use of indiarubber was forbidden, as I intended to insert ether in the silver flask and aniline in the calorimeter; and even if such had not been the case, indiarubber connexions are, at the best, unsatisfactory and unreliable. I decided, therefore, not to commence my experiments until I found that the apparatus was absolutely gas-tight in all parts; and I may mention that the greater part of last summer was unsuccessfully devoted to the endeavour to secure perfection in this respect. During last winter I spent considerable time in the effort to obtain some suitable medium by which to join glass to metal; and with the assistance of Mr. Thomas I was at last successful in procuring an alloy by which an air-tight join could be formed†, and which would stand considerable changes of temperature. Five glass tubes passed from the calorimeter to the steel lid, rendering ten such glass-to-metal joins necessary, besides several similar ones in the exterior connexions.

In the spring of this year the intramural space was exhausted until the reading of the McLeod gauge connected therewith was reduced to 11, indicating a pressure of about 0·12 millim. The apparatus was then left untouched for a month except that the temperature was occasionally raised or lowered, and at the end of that time the reading of the gauge was still less than 12. Dry air was then readmitted to this space, and the silver flask with its connected tubes (embracing about 50 feet of tubing with several joins) tested in a similar manner. Those who have had to deal with low pressures will understand that when all was found satisfactory a great difficulty had been surmounted. I did not retain this vacuum during the experiments, as I felt that it would subject the glass tubes &c. to a continuous strain which the conditions of the experiments rendered unnecessary. The labour had not been lost, however, for I was able to count with confidence on the gas-tightness of the whole apparatus.

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* A similar conclusion was arrived at by Bottomley; see Phil. Trans. 1887, A.

† Proc. Camb. Phil. Soc. 1894.

I now pass to a description of that vital part of any such investigation, viz. the thermometry. The method I proposed to adopt necessitated extremely accurate measurements of small differences of temperature. The actual elevation was of little consequence, and therefore the use of differential thermometers immediately suggested itself. Two platinum thermometers (labelled AB and CD) were constructed with great care: four stout platinum leads passed down the stem of each, supported and insulated in the usual manner by small disks of mica, and the resistance of all these leads was made as equal as possible before attaching the coils. Great attention was given to this matter, and it is safe to assume that the leads in no case differed amongst themselves by 1 in 10,000. The coils, consisting of a particularly pure sample of platinum wire, were then attached, and several days were devoted to securing their equality. Their resistance in ice was about 18 ohms: thus $\frac{1}{1800}$ of their resistance could be directly determined in the box. The galvanometer swing was about 500 for a change of ·01 in the box; and such equality was secured that when both thermometers were placed in ice (the necessary precautions being taken with regard to exterior connexions &c.), no difference in the swing of the galvanometer could be observed; thus they differed by a quantity certainly less than 1 in 100,000. This equality, although not a necessity, was a great convenience.

Although cut from the same length of wire and insulated in a precisely similar manner, the coils did not possess exactly the same coefficients. The resistances in steam and sulphur were repeatedly determined and checked by observations in the vapour of aniline. Both thermometers were on several occasions heated to a red heat, the hard glass tubes containing them becoming slightly bent in the process; but since this annealing no further change has been observable in them. The method of completely standardizing such instruments has been fully described by Professor Callendar and myself in Phil. Trans. 1891, A, and I need not therefore here dwell upon it. The values of $\delta$ differed slightly, viz. 1·513 and 1·511; but such a difference, even if not allowed for, would over the range 0° to 100° C. in no case cause an error exceeding about $\frac{1}{2000}$° C. in elevation. These thermometers were so connected that the compensating leads of AB were placed in series with the coil of CD, and *vice versâ*. Any heating of the stem of AB or CD, therefore, added an equal resistance to each arm of the bridge; and as the leads were everywhere bound together, the indications were absolutely independent of all changes in temperature except those of the bulbs.

Great care is required to accurately determine the fixed points of such thermometers. For example, a difference of 1° at 100° C. made a difference of ·067835 ohm: thus a difference of 1 millim. on the barometer caused a difference of ·00244 ohm. Readings of the pressure were taken on a standardized $\frac{3}{4}$-inch diameter mercury-barometer, and also on a compensated sulphuric barometer suspended beside it. It was found that the observations, if corrected to 100° C. by the pressure as deduced from a mercury-barometer, were not in close agreement; but if by the sulphuric-acid barometer, the results were satisfactory. On examination it appeared that the first observations of each series, when corrected for pressure, were in harmony whichever barometer was used; but such was not the case with subsequent ones of the same series. The cause is, I believe, to be found in the necessary handling of the barometer that takes place when adjusting the mercury to the ivory point. The temperature within the case undergoes a change, and the indications of the thermometer usually placed within the metal tube surrounding the barometer give but little information as to the real temperature of the mercury column, whereas the sulphuric-acid barometer requires no manipulation and is independent of such temperature changes. As an example of the consistency of the boiling-point when corrected by the $H_2SO_4$ barometer, I give the following *consecutive* results :—

(Difference in R for 1° C. at 100° = ·067835.)

| Date. | R after correction for temperature of box, plug errors, &c. | Barometer corrected to sea-level, lat. 45° and temp. 0° C. | Boiling-point. | Correction to 100° C. | $R_1$ (at 100° C.). |
|---|---|---|---|---|---|
| | | Thermometer AB. | | | |
| June 3 ... | 24·58798 | 761·10 | 100·040 | −·00271 | 24·58527 |
| „ 5 ... | 24·57187 | 754·67 | 99·802 | +·01342 | 24·58529 |
| July 7 ... | 24·58336 | 759·25 | 99·972 | +·00190 | 24·58526 |
| | | Thermometer CD. | | | |
| June 3 ... | 24·58606 | 761·10 | 100·040 | −·00271 | 24·58335 |
| „ 5 ... | 24·56961 | 754·52 | 99·796 | +·01383 | 24·58344 |
| July 7 ... | 24·58163 | 759·34 | 99·975 | +·00168 | 24·58333 |

The above examples will show that it is possible to determine the resistance at 100° C. to better than 1 part in 250,000, and nearly the same order of accuracy is obtainable, with proper precautions, in the vapour of sulphur.

I believe the most difficult point to accurately determine is freezing-point, and for really satisfactory determinations it is advisable to use distilled-water ice; but if this is manufactured in the usual manner there is great danger that some trace of salt may be carried from the freezing-mixture to the ice. One precaution I have found advantageous when using ordinary ice, viz., on adding water to the powdered ice it is advisable to use water resulting from the melting of that ice itself rather than either distilled or tap water.

I will not burden this paper with any further detailed account of the standardization of these thermometers. Between March 4th and July 7th the fixed points were determined on over 30 occasions, in ice, steam, or sulphur vapour, and no variation which would affect temperature measurements between 0° and 100° C. by as much as $\frac{1}{2000}$° C. presented itself during the latter half of these observations, the record and reductions of which alone make a large pile of manuscript.

The two thermometers, with their leads connected as described, were placed at opposite ends of a bridge wire of platinum-silver. During the spring of this year this wire was subjected to a most careful calibration by what was practically Carey Foster's method, and it proved to be more unequal than I had expected. It was therefore re-calibrated by a different method in which a resistance-box was used as a shunt, and the agreement between the results was satisfactory. The whole wire was 80 centim. long and had a total resistance of about ·4 ohm. For convenience, and to avoid thermal effects, a similar wire connected with the galvanometer was laid alongside it, and the sliding-piece was fitted with a screw so arranged that a small turn of the screw-head made contact with both wires *.

The wire and contact-maker were covered by a thick copper shield (the screw-head projecting through a narrow slit) passing from end to end of the bridge: thus the temperature of the wire was kept uniform. By means of a vernier the divisions on the scale could be read to $\frac{1}{10}$ millim., which with this wire and thermometers AB and CD indicated at 50° C. a temperature-difference of ·000915° C.† The temperature-coefficient of this wire was found to be ·00029. The resistances of the different parts of the wire were, after correction for the errors of individual coils, &c., merely expressed in terms of the mean box ohm, the absolute value being of no consequence so long as the fixed points were determined in terms of the same standard. The remaining two arms of the bridge were constructed of german-silver. They were wound together, boiled in paraffin, placed in a bottle, and I expended much care in finally adjusting them until equal. Their resistance was about 5 ohms and the galvanometer about 8 ohms, which, assuming the resistance of the thermometers as about 20 ohms each, would give nearly the maximum of sensitiveness. A single storage-cell was always

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* This method of making the connexion is due to Professor Callendar, and is exceedingly effective and convenient.

† A thicker wire giving a more open scale was tried at first, but found to be less convenient than the one finally adopted and calibrated.

used, and a resistance of 40 ohms was placed in the battery circuit when the thermometers were in ice. A table was then calculated which gave the resistance necessary in the battery circuit when the thermometers were at any temperature in order that $C^2R$ (where R is the thermometer resistance) should be constant. Thus the rise in the temperature of the thermometer coils due to current-heating was always the same, and consequent errors were eliminated, a point to which I attach considerable importance.

The value of $R_1 - R_0$ in thermometer AB was 6·88815; therefore a difference of 1 ohm at 50° C. indicated a difference of 14°·5177 C., and as

$$\frac{d\,pt}{dt} = \left\{1 - \delta\,\frac{2t-100}{100^2}\right\},\text{*}$$

the degree value of any bridge-reading at other temperatures can be deduced.

There was no difficulty, in the arrangement above described, in reading with certainty a difference of $\frac{1}{1000}$° C., and, as an illustration, I may mention the fact that if the thermometers were placed in separate hypsometers side by side on the bench and one of the hypsometers was then removed to the ground (about 3 feet below), the difference in the bridge-wire reading thus caused slightly exceeded ·4 millim.

Before leaving this portion of the subject I may mention that I carefully compared the thermometer AB with two standards from the International Bureau of Weights and Measures, which passed through my hands this summer on their way to Sydney University, and further with a separate standard sent me by the Bureau in February 1893. As the particulars of this comparison are now in the press †, I need not refer to them further than to say that the results were most satisfactory.

When the experiments were in progress the thermometer CD was placed in a hole drilled in the wall of the steel chamber parallel to the side and separated from the inner surface by only $\frac{1}{16}$ in.: thus it assumed the temperature of the walls surrounding the calorimeter. Thermometer AB passed within the calorimeter and was immersed to an inch above its bulb in the contained liquid. The reading on the bridge-wire thus gave the difference between the temperature of the calorimeter and the walls of the surrounding chamber.

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* Phil. Trans. 1891, A. p. 142.

† 'Science Progress,' September 1894

To ascertain the actual temperature and the *constancy* of the temperature of the surrounding walls, a second hole, like that already described, was drilled in the steel, in which a mercury thermometer of open scale was placed. The stem, where it protruded above the lid of the tank, was surrounded by a glass tube up which the motor pumped the tank-water, which, passing out at the top, returned to the tank. The stem, therefore, was maintained at a steady temperature, and the fluctuations observed might be considered as solely due to changes in the walls of the steel chamber. The stem of thermometer A (used at the lower temperatures) was divided into millimetres, about 27 to a degree, and No. II. (used at the higher) about 20 millim. per degree. They were observed through a telescope containing a micrometer-scale giving direct readings to $\frac{1}{10}$ of a millimetre. The tenth of one of these divisions could be estimated, and thus changes of $\frac{1}{1000}$° C. (*i.e.* about ·025 millim.) were easily observable. This was important, as the bridge-wire readings had to be corrected for any movement in the temperature of thermometer CD—that is, the temperature of the walls of the chamber.

The stirrer (which consisted of two nearly vertical narrow paddles, reaching from top to bottom of the calorimeter) was so placed as to throw the liquid across the silver flask and coil against the thermometer. This form of stirrer was not the one I should have adopted had the apparatus been designed solely for the experiments which I am now describing. In that case I should have preferred the form described in paper J, which threw the liquid from the bottom to the top of the calorimeter; and I believe that such irregularities as have presented themselves in these experiments, especially with the smallest mass, are due to insufficient stirring. When the calorimeter is full of liquid the nature of the stirring is of less consequence; and as I proposed in the experiments for which the apparatus was designed to completely fill the calorimeter, I adopted the form which it appeared to me would generate the least heat compatible with efficient mixing. The stirrer was supported in the same manner as that described in a former paper; that is, its bearings were entirely external to the calorimeter except at the base, where, to check vibration, an agate cylinder hung within a ring *.

In place of the 2000 revolutions per minute used in my former work I confined myself, for the reasons above stated, to a comparatively slow rotation of from 500 to 300 revolutions per minute. The revolving shaft was electrically connected with the chronograph in such a manner that the time of every 1000 revolutions was automatically recorded on the tape.

Before commencing the observations on aniline I introduced 299·35 grms. (*in vacuo*) of water into the calorimeter, and, with a view to ascertaining the water-equivalent, performed a few experiments to determine the rate of rise when a known current was passed through the coil. The point was not of great importance, as I proposed to determine the specific heat of aniline by a method requiring no knowledge of the water-equivalent, which, however, when the specific heat of aniline was known, could be deduced from the experiments, and thus a previous determination by means of water would serve as an independent test of the accuracy of the results. I had not covered the german-silver coil with any insulator, since, aniline being itself an insulator, the precaution was unnecessary; and this freedom to use the naked wire was one of the chief reasons which led to the adoption of aniline as a suitable liquid for my subsequent work. I was therefore aware that I could not expect very satisfactory results from the use of water. The polarization was considerable, as shown by the back E.M.F. at the termination of an experiment, and also by the difficulty experienced in making any accurate determination of the coil-resistance. However, it was subsequently found that the experiments gave very fair results.

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* A portion of the shaft of the stirrer was constructed of ivory, to diminish its thermal conductivity.

The temperature was raised from about ·5° C. below to ·5° C. above the surrounding temperature (*i. e.*, through about 12 centim. of the bridge-wire), and the times of passing the several divisions of the bridge-wire were recorded on the chronograph. Five experiments were performed, and the results of the first three gave a water-equivalent of 80·1, and Nos. 4 and 5 of 79·8. They were thus divided into groups before the results were calculated, as the coil showed decided signs of change in resistance between the two batches of experiments. I had proposed to continue these experiments with a different mass of water, but became alarmed as to the effect on the coil of the change that was going on, and decided to withdraw the water, for had the coil become useless from any cause, the whole apparatus would have had to be taken to pieces and the base of the calorimeter unsoldered, &c., involving a delay of at least a week or two.

During the time that the water was in the calorimeter I performed a considerable number of experiments to determine the rise in temperature due to the work done by the stirrer. With this form of stirrer and the low rates, $tr^2$ was practically a constant, where $t$ was the time of rising 1 centim. of the bridge-wire and $r$ the rate of revolution per second. The resulting correction was comparatively small, amounting to about $\frac{1}{25}$ of the heat generated by the current during the water-equivalent experiments; thus any small error in the correction introduced when eliminating the heat supplied by the stirrer became unimportant.

After the water was withdrawn, the whole apparatus was kept for three days at a temperature between 40° and 50° C., while dried air was forced continuously through every part of it. At the end of this time a sulphuric-acid bulb (through which the air passed on its exit from the apparatus) showed no increase in weight. I then introduced 294·99 grms. (*in vacuo*) of aniline into the calorimeter *.

I will at once state that no great pains were taken to secure an absolutely pure specimen of aniline. For my subsequent experiments the purity of the aniline was a matter of no consequence, as I only required to know the actual capacity of the calorimeter and contents at different temperatures.

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* The precautions observed in order that the mass introduced might be accurately determined are fully described in paper J, p. 418.

Again, as regards the purposes of this investigation I think that it will be of greater service if I am able to supply experimenters with the specific heat of a quality of aniline at all times procurable, rather than if I gave the constants of a quality only to be obtained with difficulty. The sample I used was supplied by Messrs. Harrington Bros., as "pure colourless," and had but a light brown tinge. It was redistilled by me once before use, and I also determined its boiling-point, which was in agreement with that of a specially pure sample which I had examined on a previous occasion *. Further (and this I have always found to be a fair test of the purity), the temperature of the boiling-point did not change during distillation.

From the time that aniline was first introduced into the calorimeter all signs of polarization disappeared, and the insulation of the coil was very perfect.

I will now describe the method of conducting an experiment.

The tank was first brought to the desired temperature, and the experiment was not proceeded with until the tank-temperature had had time to become steady. Freshly distilled ether was then introduced into the silver flask, and dried air passed through it (the stirrer in the surrounding aniline being continually at work) until the *whole* of the ether was evaporated. The taps connected with the silver flask were then closed, the key inserted in the storage-circuit, the connexion with the Clark cells made, and the rheochord adjusted until the potential-difference at the ends of the coil was shown by the high-resistance galvanometer to be equal to that of the Clark cells used. Three or four of these cells were placed in parallel arc, and the files thus formed in series : therefore, when using an electromotive force of 4 Clark cells, we had really in use 12 or 16.

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* Trans. 1891 A, p. 64.

Throughout an experiment the attention of my assistant[*] was directed to keeping the potential balance as even as possible. I meanwhile had to observe and mark the time of transit across the graduations of the bridge-wire. A reversing-key was maintained at a constant period of oscillation (about twice per second), and as the temperature rose the oscillations of a dead-beat galvanometer mirror (which were viewed through a telescope fitted with a micrometer-scale) steadily diminished, and the moment when they ceased could, to my surprise, be determined with great accuracy. By pressing a key, the time was recorded on the chronograph tape.

The mercury-thermometer inserted in the walls of the steel chamber was observed at regular intervals, any alteration noted, and a correction afterwards applied to the bridge-wire reading—the value of each division of the bridge-wire in terms of a millimetre of the thermometer-scale being known. The time of each 1000 revolutions of the stirrer was automatically recorded on the tape: thus the only notes that had to be taken during an experiment were of the changes of the mercury-thermometer. The chronograph was one of somewhat novel construction, for which I am indebted to Mr. E. A. Pochin. It was worked by a water motor, had a triple set of recording hammers, and was controlled by an electric clock which was compared at regular intervals with a "rated" Dent's chronometer, but as the greatest gain in rate observed was less than 1 in 12,000, no correction was necessary.

I find it impossible to give a detailed record of the observations, as it would fill a volume. I therefore propose to give an example in full of one of the experiments by drawing at random one of the leaves from the mass of records. (Table I. p. 250.)

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[*] I take this opportunity of returning my thanks to Mr. C. Green, Scholar of Sidney College, Cambridge, for his able assistance during these experiments.

## TABLE I.

Aniline Exp. No. 26 : 4 cells. July 28th.

Cooled to reading 36 cm. b.w. Temp. of b.w. = 67°·5 F.
Temp. Clark Cells = 15°·27 C. throughout.

Experiment commenced at 1–17–30.

| Bridge-wire reading in centims. | Time by chronograph. | Number of revolutions. | Time. | Time per 1000 revolutions. | Temp. by thermometer A. |
|---|---|---|---|---|---|
| | secs. | | secs. | secs. | millim. |
| 54·5 | 331·4 | | | | 166·53 |
| 55·0 | 347·7 | 0 | 348·1 | | |
| 55·5 | 366·9 | | | | |
| 56·0 | 384·4 | | | | |
| 56·5 | 403·4 | | | 204·5 | 166·55 |
| Mean ...... | 366·8 | | | | |
| 61·5 | 582·5 | 1000 | 552·6 | | 166·58 |
| 62·0 | 600·5 | | | | |
| 62·5 | 619·4 | | | | |
| 63·0 | 638·1 | | | 204·6 | |
| 63·5 | 656·0 | | | | 166·60 |
| Mean ...... | 619·3 | | | | |
| 68·0 | 819·9 | 2000 | 757·2 | | 166·61 |
| 68·5 | 838·5 | | | | |
| 69·0 | 856·2 | | | 204·2 | |
| 69·5 | 874·9 | | | | |
| 70·0 | 892·6 | 3000 | 961·4 | | 166·60 |
| Mean ...... | 856·4 | | | | |
| 75·0 | 1079·6 | | | 205·3 | 166·60 |
| 75·6 | 1098·7 | | | | |
| 76·0 | 1118·3 | | | | |
| 76·5 | 1137·4 | | | | |
| 77·0 | 1156·2 | 4000 | 1166·7 | | 166·59 |
| Mean ...... | 1118·0 | | | | |

Mean reading of thermometer A = 166·58 millim. = 16°·459 C.

### *Reduction of the Results.*

Let $\theta_0$ be the temperature of the surrounding envelope and $\theta_1$ that of the calorimeter at any time $t$. Let the change in temperature per second due to the work done by the stirrer be $\sigma$, and let $\rho$ equal the gain in temperature per second due to the combined effects of convection, conduction, and radiation when the difference in temperature between the calorimeter and the surrounding envelope is unity.

Let a wire whose resistance is R at $\theta_0$ and $R_1$ at $\theta_1$ be immersed in a liquid contained in the calorimeter, and let the mass of the contained liquid be M and its specific heat $S_1$ when the temperature is $\theta_1$.

Let the capacity for heat of the calorimeter be $w_1$ when the temperature is $\theta_1$.

Thus the thermal capacity of the calorimeter and contents at any temperature $\theta_1$ is $S_1M+w_1$.

If the ends of the wire be kept at a constant potential-difference of E, then we get (paper J, p. 367) :—

$$\frac{E^2}{J\,.\,R_1(S_1M+w_1)}+\{\sigma-\rho(\theta_1-\theta_0)\}=\frac{d\theta_1}{dt}.$$

Since $\sigma$ is small and we can make $\theta_1-\theta_0$ of any magnitude we please, it is always possible to obtain a value of $\theta_1$ such that $\sigma-\rho(\theta_1-\theta_0)=0$; and in that case

$$\frac{E^2}{J\,.\,R_1(S_1M+w_1)}=\left(\frac{d\theta_1}{dt}\right)_e,$$

the suffix denoting the nature of the supply.

This temperature (viz. that value of $\theta_1$ which causes $\sigma-\rho(\theta_1-\theta_0)$ to vanish) I shall denote throughout this paper by the term "null point," by which I mean that value of $\theta_1$ at which the observed rate of rise is due to the electrical supply only, and I shall use $\theta_N$ to indicate that temperature.

Two or three methods of finding $\theta_N$ suggest themselves. If the stirrer be set working when there is no electrical supply, then $\theta_1$ will gradually approximate to $\theta_N$, and a few observations as to the rate of change in $\theta_1$ will supply sufficient information to enable the observer to set the value near to

$\theta_N$, and the calorimeter can then be left to gradually assume the true value. I have given this method a fair trial, for the apparatus has been left working for twenty-four hours at a time, and the value of $\theta_N$ ascertained with precision.

For example, at the rate of 9·10 revolutions per second it was found that the value of $\theta_N - \theta_0$ (expressed in terms of the mean bridge-wire centimetre) was about 9·2 (*i. e.* 0°·85 C. approximately), and that when the rate was 5·00 the value was about 2·7 (=0°·25 C. approximately); and it is noticeable that the ratio 9·2 : 2·7 is nearly that of $(9{\cdot}1)^2 : (5{\cdot}0)^2$, thus indicating that the heat developed by the stirrer varied approximately as $r^2$, where $r$ is the rate of revolution.

A modification of this method renders it possible to determine the thermal value of the stirring work. After obtaining $\theta_N$ as above, find what value of $\theta_1$ will cause the temperature to remain steady when the heating effect is that due to the stirring and a potential-difference of one Clark cell. Call this temperature $\theta_{N_e}$; we have thus two equations,

$$\sigma - \rho(\theta_N - \theta_0) = 0,$$

and

$$\sigma + \frac{e^2}{J \,.\, R_1(S_1M + w_1)} - \rho(\theta_{N_e} - \theta_0) = 0\,;$$

hence

$$\frac{\sigma}{\sigma + \dfrac{e^2}{J \,.\, R_1(S_1M + w_1)}} = \frac{\theta_N - \theta_0}{\theta_{N_e} - \theta_0}.$$

Whatever method is adopted the experiments involve much labour and time, for a redetermination of $\theta_N$ must be made for each change in $\theta_0$, as it is probable that owing to changes in the viscosity and surface-friction of the contained liquid, $\theta_N$ would be some function of $\theta_0$ when the rate of revolution of the stirrer is constant; and a complete determination of the value of $\theta_N$ for each value of $\theta_0$ would have doubled or trebled the length of the investigation.

It has always appeared to me to be possible that the value of $\rho$ is a function of the rate of change in the temperature of the calorimeter. The temperature-gradient from the calorimeter to the surrounding walls must alter slightly with the rate of change in $\theta_1$, and the rate of loss or gain in temperature of the calorimeter must as a consequence be affected; or, in other words, I think it probable that the value of $\theta_N$ is a function of $\frac{d\theta_1}{dt}$, hence the value of $\theta_N$ obtained by experiments such as those described above, where the temperature of the calorimeter is constant, may differ appreciably from the value of $\theta_N$ when the temperature is rising.

The method I finally adopted must diminish, although it does not entirely eliminate, any error due to this change in $\theta_N$.

Let several experiments be performed similar in all respects except that the potential-difference is changed in each case.

Let the potential-difference of a Clark cell be $e$, and let $n$ be the number of cells used.

Then

$$\frac{(ne)^2}{JR_1(S_1M+w_1)}+\{\sigma-\rho(\theta_1-\theta_0)\}=\frac{d\theta_1}{dt};$$

hence

$$\left(\frac{d\theta_1}{dt}\right)\times\frac{1}{n^2}=\frac{e^2}{JR_1(S_1M+w_1)}+\frac{\sigma-\rho(\theta_1-\theta_0)}{n^2}.$$

Let us assume for the time that $\theta_N$ is independent of $n$, then, when $\theta_1=\theta_N$, we get

$$\frac{d\theta_N}{dt}\times\frac{1}{n^2}=\frac{e^2}{JR_1(S_1M+w_1)};$$

hence

$$\frac{d\theta_N}{dt}\times\frac{1}{n_1^2}=\frac{d\theta_N}{dt}\times\frac{1}{n_2^2}=\frac{d\theta_N}{dt}\times\frac{1}{n_3^2}=\text{\&c.}$$

where $n_1$, $n_2$, $n_3$ &c. are the number of cells used in each case.

If, therefore, we plot the curves (which in this case are straight lines since the variables, viz., $\rho(\theta_1-\theta_0)$ and $R_1$, $S_1$, and $w_1$ may for small changes of temperature be considered as linear functions of $\theta_1$, see paper J, pp. 442–448), which we obtain by taking $\frac{d\theta_1}{dt}\times\frac{1}{n^2}$ as ordinate, and $\theta_1$ as abscissa, they will intersect where the abscissa is $\theta_N$, and there only; and since the value of $\frac{d\theta_1}{dt}$ can be experimentally determined for different values of $\theta_1$, the observations themselves can be made to give the value of $\theta_N$, and we can thus find $\frac{e^2}{J.R_1(S_1M+w_1)}$, the rise due to the electrical supply alone.

A small deviation from the true value of $\theta_N$ is of little consequence, for the resulting value of $\frac{d\theta_1}{dt}\times\frac{1}{n^2}$ will only differ from $\frac{d\theta_N}{dt}\times\frac{1}{n^2}$ by the quantity $\frac{\rho(\theta_1-\theta_N)}{n^2}$, and since $\rho$ is small as compared with the other magnitudes, $\theta_1-\theta_N$ must be considerable before the error becomes appreciable.

As this is an important point, I will select one of the three-cell experiments (No. 37) in order to show the relative magnitude of the various quantities, and the probable limit of error arising from the assumption that $\theta_N$ is independent of $n$. The differences in temperature are expressed in terms of the temperature difference equivalent to 1 centim. of the bridge-wire, but would of course have the same relative values in any scale.

$$\rho=\cdot000082.$$

$$\sigma=\cdot000230.$$

$$\left(\frac{d\theta_N}{dt}\right)=\cdot014670.$$

Let us assume that the value taken for $\theta_N$ differed from the true value by as much as 1 bridge-wire degree (as will be seen when the experimental results are given, this is an excessive estimate), then $\theta_1-\theta_N=1$, hence (*supra*) the value of $\frac{d\theta_1}{dt}$ would differ from

$$\frac{d\theta_N}{dt} \text{ by } \frac{\rho(\theta_1-\theta_n)}{n^2}=\frac{\cdot000082\times1}{9}=\cdot000009.$$

When the values of $\frac{d\theta_1}{dt}=\frac{1}{n^2}$ (where $n=2, 3,$ or $4$) were plotted as ordinates with $\theta_1$ as abscissa, the resulting straight lines were found to intersect not in one but in three points, which, however, were so near to each other that (except in one case) the probable error introduced by assuming that any one intersection gave the true value of $\theta_N$ was less than that above indicated. The triangle formed by joining the three points of intersection was almost invariably of one form and of nearly equal dimensions, indicating that its existence was not due to experimental irregularities but was connected in some way with the difference in the rate of rise with different values of $n$. I think that my impression that $\rho$ and hence $\theta_N$ are functions of $\frac{d\theta_1}{dt}$ is thus confirmed.

In any case the error caused by the assumption that $\theta_N$ is the same with different rates of increase in temperature, must be less than the error resulting from the assumption that it is the same when the temperature is rising and when it is steady.

Again, the null point finally selected for each group of experiments was always obtained in the same manner from the three points of intersection. Any error, therefore, is of the same nature in each case, and as the specific heat was obtained by the subtraction of one ordinate from another, the effect of any error is diminished considerably. True, when the absolute value of the ordinate is used in order to obtain the water equivalent of the calorimeter, any error in the position of $\theta_N$, and therefore in the length of the ordinate, would produce its full effect, and might be appreciable, but as regards the determination of the specific heat by the method of differences it is almost certainly negligible. It would be represented by $\frac{(\rho_1-\rho_2)(\theta_1-\theta_N)}{n^2}$, where $\rho_1$ and $\rho_2$ are the values of $\rho$ when the masses of the liquid are $M_1$ and $M_2$; and since

$$\rho_1(M_1S_1+w_1)=\rho_2(M_2S_1+w_1),$$

the limit of error is given by the expression

$$\frac{\rho_1S_1(M_2-M_1)}{M_2S_1+w_1}\times\frac{\theta_1-\theta_N}{n^2}.$$

Now the value of $\frac{S_1(M_2-M_1)}{M_2S_1+w_1}$ in these experiments was about $\frac{1}{4}$, hence we get $\frac{\rho_1}{4}\cdot\frac{\theta_1-\theta_N}{n^2}$ as the expression for the error, and this would in no case amount to $\frac{1}{1000}$ of $\frac{d\theta_N}{dt}$.

I assume, therefore, that the values of $\frac{d\theta_N}{dt}$ given by the experiments are sufficiently approximate.

If $C_b$ is the value, in degrees C. of the air-thermometer, of the temperature difference equivalent to 1 centim. of the bridge-wire[*], then

$$\frac{d\theta_N}{dt} \times \frac{R_1 \times C_b}{e^2}$$

gives the rise per second in degrees C. with unit resistance and unit potential-difference.

The reciprocal of the quantity thus found gives us T, the time of rising 1°, when $E=1$ and $R=1$.

Now

$$\frac{T}{J} = \sigma_1 M + w_1.$$

Let the value of T be $T_1$ when M is $M_1$, and $T_2$ when M is $M_2$.

Then we get

$$S_1 M_1 + w_1 = \frac{T_1}{J},$$

and

$$S_1 M_2 + w_1 = \frac{T_2}{J},$$

hence

$$S_1 = \frac{T_1 - T_2}{J(M_1 - M_2)}.$$

We can now find the value of $S_1 M_1$, and therefore

$$w_1 = \frac{T_1}{J} - S_1 M_1.$$

Thus both the specific heat of the liquid and the water-equivalent can be found if two groups of experiments with different masses of liquid have been performed at the same temperature.

Since $J = 4{\cdot}198 \times 10^7$[†] ergs, when the unit of heat is "the quantity of heat required to raise 1 grm. of water through 1° C. of the air-thermometer at 15° C.," it follows that the results obtained at different temperatures are all expressed in terms of that unit, and are not dependent upon our knowledge of the changes in the specific heat of water.

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[*] See p. 243, *supra*.

[†] Proc. Roy. Soc. lv. p. 26.

### *Corrections.*

Before proceeding to plot the results the following corrections had to be made :—

I. For changes in the temperature of the steel chamber during the time of an experiment. For temperatures below 26° C. a mercury-thermometer labelled A was used, situated as described on p. 245, and 1 millim. change in A was equivalent to 4·05 millim. in the bridge-wire reading. Thermometer II. was used for temperatures above 26° C., and 1 millim. change in II. was equivalent to 5·5 millim. of the bridge-wire. The resulting correction had to be added or subtracted from the bridge-wire value of $d\theta_1$, and it rarely exceeded 0·2 millim.

II. The correction to the "mean bridge centimetre." This correction was given with great exactness by the table resulting from the calibration of the bridge-wire previously referred to. It is applied as a factor to $\frac{d\theta_1}{dt}$.

III. The normal rate of stirring during experiments 1 to 8 was 9·10 revolutions per second, for the remaining experiments 5·00. A considerable number of experiments gave $tr^2 = 800{,}000$ approximately, where $r$ is the rate per second, and $t$ the time of rising 1 centim. of the bridge-wire. The correction to the normal rate therefore is $\frac{r^2 - r_1^2}{800{,}000}$, where $r$ is the normal and $r_1$ the observed rate.

As the stirring rarely departed much from the normal this correction was always small, it in no case exceeded ·00006, and rarely exceeded ·00002 ; and as the values of $tr^2$ given by the stirring experiments did not differ by more than 1 part in 50, the correction is sufficiently close.

IV. The correction consequent on changes in the temperature of the bridge-wire. This is given with sufficient accuracy by the expression

$$\frac{d\theta_1}{dt} \times \{1 + \cdot 00016(\theta_1 - 59)\},$$

$\theta_1$ being measured by a Fahrenheit thermometer.

V. The correction for the temperature of the Clark cells. Assuming Lord Rayleigh's temperature-coefficient ·00077, we get $\frac{d\theta_1}{dt}\{1+{\cdot}00154(\theta-15)\}$; for the rate of rise varies as $E^2$.

VI. The subsequent operations are simplified if some arbitrary value is assigned to R′, and the consequent value of $\frac{d\theta_1}{dt}$ for that value of R′ ascertained. As the resistance of the coil increased from about 8·45 to 8·6 ohms as $\theta_1$ increased from 15° to 50° C., it was found convenient to take 8·5 ohms as the arbitrary resistance. The correction is $\frac{d\theta_1}{dt} \times \frac{R_1}{8{\cdot}5}$.

The true value of $R_1$, however, is not that obtained by merely taking the resistance in the usual manner with a small current. I have in paper J, pp. 404–7, published a full account of a method of finding the increase in R′ due to an increase in the potential-difference of 1, 2, &c. Clark cells.

The increase, with this coil, was carefully determined, with the following results*:—

TABLE II.

| Potential-difference (in terms of a Clark cell). | δR (in true ohms). |
|---|---|
| 1 | ·00087 |
| 2 | ·00227 |
| 3 | ·00433 |
| 4 | ·00723 |

The resistance of the coil was carefully determined for each group of experiments, at the mean temperature of the group, and also occasionally at a fixed temperature, in order to trace any change. During the first series a slight increase was observable (apart from the natural increase due to its temperature-coefficient). This was possibly a consequence of an oversight on my part, as I had forgotten to previously anneal the wire. After it had been raised to the highest temperature attained during these experiments, the further change became negligible.

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* I have to thank Mr. F. H. Neville, Fellow of Sidney College, Cambridge, for his kindness in assisting me in this somewhat troublesome determination.

The absolute value of $R_1$ was obtained by means of the dial-box described in paper J, pp. 408–10. The errors of the separate coils and of the coils in the bridge-arms had been ascertained by a direct comparison, which had been made by kind permission of Mr. Glazebrook, with the B.A. standards in the autumn of 1892.

VII. The value of $\frac{d\theta_1}{dt}$ at several points of the range (which was usually about 15 centim. of the bridge-wire, *i. e.* about $1^{\circ}{\cdot}4$ C.) having been ascertained, the results were plotted (with $\theta_1$ as abscissa) in order to ascertain the regularity &c. of the observations, which was generally found to be satisfactory. The values of $\frac{d\theta_1}{dt}$ at the readings 60 and 70 of the bridge-wire were then obtained and divided by $n^2$. Three experiments having been performed at each temperature with three different values of $n$, the intersection of the three lines thus found gave $\theta_N$, the ordinate for that abscissa giving the rate of rise due to the electrical supply alone. A plan of these intersections is given on Plate VIII.

A glance at Plate VIII. will show that the null point in each case is not accurately defined.

The intersection of the 3- and 4-cell lines is always to the left of the other intersections.

I have shown (p. 255) that the error introduced by this uncertainty is in any case small, more especially so as the results are deduced from differences in the ordinates. The most probable position appears to me to be about midway between the points of intersection of the 2-cell line with the other lines; but as it is improbable that the position of the point would vary capriciously as the temperature rose, I have selected points on the smoothed curve (called the "null-point curve") which passes most nearly through the various intersections.

It will be noticed that the null-point curve approaches more nearly to the outside temperature as the value of $\theta_1$ increases[*]. This indicates either (1) that the work done by the stirrer had diminished (this would probably be due to diminished viscosity or surface friction); or (2) that the loss by convection, &c., had increased. The former is I think the more probable explanation.

When the depth of the liquid is increased, the stirrer has more work to do and the supply of heat is greater while the loss remains unchanged. The null point therefore is at a higher elevation when the mass is greater, and Pl. VIII. shows that $\theta_N - \theta_0$ is nearly proportional to the depth, *i.e.* to the mass, of the contained liquid.

In order to illustrate the method of applying the various corrections, and also to indicate their comparative magnitude, I give in full (Table III.) the working out of experiment 26, of which the details were given in Table II. The numbers in Roman numerals indicate the sections on the preceding pages, in which the particulars of the correction are given. The greatest correction is that given by the calibration of the bridge-wire, and this can be applied with great certainty.

I do not consider it necessary to crowd this paper with similar details regarding the remaining experiments. Table IV. (pp. 262, 263) is a summary in which I have given the numbers necessary for the remaining calculations.

[*] This curvature is more marked than would at first sight appear from an inspection of Plate VIII. Owing to the difference in the temperature-coefficient of the two differential thermometers, the true bridge null point is given by the expression $59{\cdot}84 + {\cdot}0003\,\theta_1$, where $\theta_1$ is the temperature of the thermometers. The position of the bridge null point is shown by the vertical lines on the left.

## TABLE III.

### Showing the Corrections necessary for the Reduction of Experiment 26. July 28.

| | Range on bridge-wire 55·5–62·5 cm. | Range on bridge-wire. 62·5–69·0 cm. | Range on bridge-wire. 69·0–76·0 cm. | Ref. No. |
|---|---|---|---|---|
| Observed time over range ($t$) ...... | 252·5 secs. | 237·1 secs. | 261·6 secs. | |
| Change in external temp. (therm. A) during the experiment ............ | +·05 mm. | +·015 mm. | −·010 mm. | |
| Change in range consequent on change in therm. A (1 mm. A = 4·05 mm. of bridge-wire) ......... | +·020 cm. | +·006 cm. | −·004 cm. | I. |
| Uncorrected rise per 1 sec., *i. e.* $\frac{d\theta_1}{dt}$ | ·027802 | ·027440 | ·026743 | |
| Mean value of 1 cm. of the bridge-wire over this range in terms of mean bridge-wire cm. ............ | 1·00245 | ·99281 | ·99494 | |
| Correction of $\frac{d\theta_1}{dt}$ to mean bridge-wire cm. | +·000068 | −·000197 | −·000135 | II. |
| ,, ,, for temp. of Clark cells. | +·000010 | +·000010 | +·000009 | V. |
| ,, ,, for temp. of bridge-wire. | +·000037 | +·000037 | +·000036 | IV. |
| ,, ,, for stirring to rate 5·00. | +·000012 | +·000011 | +·000011 | III. |
| $\frac{d\theta_1}{dt}$ after corrections .................. | ·027929 | ·027301 | ·026664 | |
| Mean point of range (bridge-wire)... | 59·00 | 65·75 | 72·50 | |
| | A. | B. | C. | |

Since the points thus found should lie on a straight line, the best result is arrived at by treating the results so as to obtain 2 points only. If we mean A and B, and again B and C, we attach undue value to B. The true mean is obtained by

$$\frac{2A+B}{3} \text{ and } \frac{B+2C}{3}.$$

We thus get:—

| | | |
|---|---|---|
| Bridge-wire readings ......... | 61·25 cm. | 70·25 cm. |
| Mean value of $\frac{d\theta_1}{dt}$ ............ | ·027720 | ·026877 |

We can thus obtain (either arithmetically or by plotting) the values of

| | | |
|---|---|---|
| $\frac{d\theta_1}{dt}$ at B.W. readings .................. | 60·00 cm. | 70·00 cm. |
| which are ................................ | ·027837 | ·026900 |

Now the value of $R_1$ near the "null point" (about 62·5 b.w.) was found to be 8·46093 true ohms. To this add ·00720 for the rise in resistance due to a potential-difference of 4 Clark cells (Table II.); hence $R_1 = 8·4681$, hence correction to $R = 8·5000$ is $-·000104$ ............................................ VI.

| | | |
|---|---|---|
| Hence $\frac{d\theta_1}{dt}$ at B.W. readings ......... | 60·00 cm. | 70·00 cm. |
| when R is 8·5000, = .................. | ·027733 | ·026796 |
| and $\frac{d\theta_1}{dt} \times \frac{1}{4^2}$ = ........................ | ·001733 | ·001675 |

## TABLE IV.

| Expt. | Date. | Mass of Aniline (*in vacuo*). | Number of cells. ($n$.) | Normal rate of stirring. | Mean external temp. C. | Temp. of "null point" above exterior. ($\theta_n - \theta_1$.) | External temp. + diff. to "null point." ($\theta_n$.) | $\frac{d\theta_1}{dt} \times 10^6$ after corrections I., II., III., IV., V., VI. at 60 b.w. | 70 b.w. | $\frac{d\theta_1}{dt} \times \frac{1}{n^2} \times 10^6$. (Plate VIII.) at 60 b.w. | 70 b.w. | Reading on "null-point" curve. | Mean value $\frac{d\theta_n}{dt} \times 10^6$. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1, 2, & 3. | July 12 | 294·99 | 3 | 9·10 | 16·935 | +·844° | 17·847 | 25672 | 24296 | 2853 | 2700 | 2747 | 2748 |
| 4 & 5. | „ 13 | „ | 2 | „ | 16·908 | +·844 | 17·720 | 11935 | 11585 | 2984 | 2646 | 2750 | |
| 6 & 7. | July 16 | 358·20 | 3 | 9·10 | 25·072 | +·862 | 25·934 | 22929 | 21397 | 2547 | 2377 | 2390 | 2392 |
| 8. | „ 16 | „ | 2 | „ | 25·069 | +·862 | 25·931 | 10656 | 9485 | 2664 | 2371 | 2393 | |
| 9. | „ 24 | „ | 2 | 5·00 | 16·375 | +·184 | 16·559 | 9923 | 8617 | 2481 | 2154 | 2417 | 2417 |
| 10 & 11. | „ {17<br>24 | „ | 3 | „ | 16·380 | +·184 | 16·564 | 21998 | 20763 | 2444 | 2296 | 2415 | |
| 12. | „ 18 | „ | 4 | „ | 16·379 | +·184 | 16·563 | 38973 | 37732 | 2436 | 2358 | 2420 | |
| 13. | „ 18 | „ | 3 | „ | 25·236 | +·184 | 25·420 | 21735 | 20476 | 2419 | 2275 | 2391 | 2395 |
| 14. | „ 18 | „ | 2 | „ | 25·351 | +·184 | 25·535 | 9787 | 8677 | 2447 | 2169 | 2395 | |
| 15. | „ 18 | „ | 4 | „ | 25·274 | +·184 | 25·458 | 38658 | 37348 | 2415 | 2334 | 2400 | |
| 16. | „ 20 | „ | 2 | „ | 32·979 | +·183 | 33·162 | 9717 | 8448 | 2429 | 2112 | 2370 | 2370 |
| 17. | „ 20 | „ | 3 | „ | 32·977 | +·183 | 33·160 | 21496 | 20255 | 2394 | 2256 | 2370 | |
| 18. | „ 20 | „ | 4 | „ | 32·968 | +·183 | 33·151 | 38168 | 36858 | 2385 | 2303 | 2370 | |
| 19. | „ 21 | „ | 3 | „ | 40·349 | +·183 | 40·532 | 21127 | 19849 | 2367 | 2222 | 2340 | 2345 |
| 20. | „ 21 | „ | 2 | „ | 40·368 | +·183 | 40·551 | 9602 | 8357 | 2401 | 2089 | 2348 | |
| 21. | „ 21 | „ | 4 | „ | 40·379 | +·183 | 40·562 | 37885 | 36475 | 2366 | 2280 | 2348 | |
| 22. | „ 22 | „ | 3 | „ | 50·225 | +·182 | 50·407 | 20726 | 19496 | 2336 | 2198 | 2311 | 2314 |
| 23. | „ 22 | „ | 2 | „ | 50·214 | +·182 | 50·396 | 9452 | 8256 | 2363 | 2064 | 2312 | |
| 24. | „ 22 | „ | 4 | „ | 50·211 | +·182 | 50·391 | 37317 | 36057 | 2332 | 2253 | 2318 | |

Table IV. (*continued*).

| Expt. | Date. | Mass of Aniline (*in vacuo*). | Number of cells ($n$.) | Normal rate of stirring. | Mean external temp. C. | Temp. of "null point" above exterior. ($\theta_N - \theta_1$.) | External temp. + diff. to "null point." ($\theta_N$). | $\frac{d\theta_1}{dt} \times 10^6$ after corrections I., II., III., IV., V., VI. at |  | $\frac{d\theta_1}{dt} \times \frac{1}{n^2} \times 10^6$. (Plate VIII.) at |  | Reading on "null-point" curve. | Mean value $\frac{d\theta_N}{dt} \times 10^6$. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |  | 60 b.w. | 70 b.w. | 60 b.w. | 70 b.w. |  |  |
| 25. | July 28 | 569·53 | 3 | 5·00 | 16·448 | +·241 | 16·689 | 15665 | 14834 | 1741 | 1648 | 1710 | 1711 |
| 26. | „ 28 | „ | 4 | „ | 16·459 | +·241 | 16·700 | 27733 | 26796 | 1733 | 1675 | 1713 |  |
| 27. | „ 28 | „ | 2 | „ | 16·484 | +·241 | 16·725 | 7135 | 6196 | 1784 | 1549 | 1710 |  |
| 28. | „ 28 | „ | 2 | „ | 25·216 | +·237 | 25·453 | 7050 | 6230 | 1763 | 1558 | 1695 | 1696 |
| 29. | „ 29 | „ | 3 | „ | 25·219 | +·237 | 25·456 | 15557 | 14627 | 1729 | 1325 | 1696 |  |
| 30. | „ 29 | „ | 4 | „ | 25·217 | +·237 | 25·454 | 27426 | 26460 | 1714 | 1654 | 1696 |  |
| 31. | „ 29 | „ | 2 | „ | 32·985 | +·236 | 33·221 | 6966 | 6142 | 1742 | 1536 | 1679 | 1680 |
| 32. | „ 31 | „ | 4 | „ | 32·999 | +·236 | 33·235 | 27245 | 26183 | 1703 | 1643 | 1684 |  |
| 33. | „ 31 | „ | 3 | „ | 32·999 | +·236 | 33·235 | 15398 | 14412 | 1711 | 1601 | 1678 |  |
| 34. | Aug. 1 | „ | 2 | „ | 40·313 | +·232 | 40·545 | 6890 | 6067 | 1722 | 1517 | 1663 | 1664 |
| 35. | „ 1 | „ | 3 | „ | 40·313 | +·232 | 40·545 | 15222 | 14296 | 1691 | 1588 | 1662 |  |
| 36. | „ 1 | „ | 4 | „ | 40·313 | +·232 | 40·545 | 26983 | 25898 | 1686 | 1619 | 1666 |  |
| 37. | „ 2 | „ | 3 | „ | 50·302 | +·228 | 50·530 | 15015 | 14053 | 1668 | 1561 | 1639 | 1640 |
| 38. | „ 2 | „ | 2 | „ | 50·274 | +·228 | 50·502 | 6804 | 5959 | 1701 | 1489 | 1640 |  |
| 39. | „ 2 | „ | 4 | „ | 50·312 | +·228 | 50·540 | 26535 | 25600 | 1658 | 1600 | 1641 |  |
| 40. | „ 3 | „ | 3 | „ | 16·522 | +·240 | 16·762 | 15701 | 14806 | 1745 | 1645 | 1712 | 1712 |
| 41. | „ 3 | „ | 4 | „ | 16·549 | +·240 | 16·789 | 27708 | 26766 | 1732 | 1673 | 1712 |  |
| 42. | „ 3 | „ | 2 | „ | 16·532 | +·240 | 16·772 | 7120 | 6200 | 1780 | 1555 | 1713 |  |

The value of $\frac{d\theta_N}{dt}$ having been ascertained as above indicated, the capacity for heat of calorimeter and contents is easily deduced.

The operations are shown in Table V.

Col. I. gives the temperature of the null point in degrees C. of the air-thermometer (from Table IV.).

„ II. the rate of rise at the null point as deduced from the group of experiments at that temperature (from Table IV.).

„ III. the value of the mean centimetre of the bridge-wire at the temperature of the null point, denoted by $C_b$.

„ IV. gives the rate of rise when $R=1$ true ohm and the potential-difference 1 volt ($e=1{\cdot}4342$, $e^2=2{\cdot}0570$), expressed in degrees C. of the air-thermometer. The value of R′ used in this reduction is 8·4966 instead of the 8·5 ohms which was selected as a convenient arbitrary value of R′ in the reductions in Table IV. The two wires connecting the roof of the calorimeter with the steel lid had a total resistance of ·0068 ohm. We may assume that half the heat generated in these wires passed into the steel lid, and half into the calorimeter. We may therefore consider their resistance as ·0034 ohm $=r$. Now the points which were kept at a constant P.D. were at the lid of the calorimeter and between these wires and the coil. The equation is $J.H.=\frac{E^2}{R_1}\left(1+\frac{r}{R_1}\right)t$; hence the effective resistance $R_1-r=8{\cdot}5-{\cdot}0034$.

„ V. gives the reciprocals of the numbers in Col. IV.

„ VI. The value of J is assumed as 4·198 *. The numbers in this column give the capacity for heat of calorimeter and contents expressed in terms of "a thermal unit at 15° C." The results when plotted as ordinates, with $\theta_1$ as abscissa, are shown in Plate IX (A).

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* Proc. Roy. Soc. vol. lv. p. 24 (1894).

## TABLE V.

| Experiments. | I. | II. | III. | IV. | V. | VI. |
|---|---|---|---|---|---|---|
| | $\theta_N$. | $\frac{d\theta_N}{dt}\times 10^6$. | $C_b$. | $\frac{d\theta_N}{dt}\times\frac{R'\times C_b}{e^2}\times 10^7$. | T. | $\frac{T}{J}$. |
| 1 to 5 ... | 17·784 | 2748 | ·09040 | 10265 | 974·2 | 232·05 |
| 6 to 8 ... | 25·933 | 2392 | ·09062 | 8952 | 1117·0 | 266·08 |
| 9 „ 12 ... | 16·562 | 2417 | ·09037 | 9020 | 1108·6 | 264·10 |
| 13 „ 15 ... | 25·471 | 2395 | ·09061 | 8964 | 1115·6 | 265·77 |
| 16 „ 18 ... | 33·158 | 2370 | ·09081 | 8890 | 1124·9 | 267·97 |
| 19 „ 21 ... | 40·548 | 2345 | ·09102 | 8816 | 1134·3 | 270·22 |
| 22 „ 24 ... | 50·398 | 2314 | ·09129 | 8722 | 1146·5 | 273·12 |
| 25 to 27 ... | 16·705 | 1711 | ·09037 | 6387 | 1565·7 | 372·99 |
| 28 „ 30 ... | 25·454 | 1696 | ·09061 | 6348 | 1575·3 | 375·30 |
| 31 „ 33 ... | 33·230 | 1680 | ·09082 | 6300 | 1587·1 | 278·10 |
| 34 „ 36 ... | 40·545 | 1664 | ·09102 | 6251 | 1599·8 | 381·11 |
| 37 „ 39 ... | 50·524 | 1640 | ·09129 | 6185 | 1616·8 | 385·14 |
| 40 „ 42 ... | 16·780 | 1712 | ·09037 | 6390 | 1564·9 | 372·80 |

### *Remarks on Tables IV. and V.*

*Experiments* 1 *to* 3 (3 *cells*) *and* 4 *to* 5 (2 *cells*) were performed with a view to testing the working of the various portions of the apparatus, and in order to ascertain the minimum quantity of liquid that could be used with safety. The results were not satisfactory: the values of $\frac{d\theta_1}{dt}$ at the same temperature, when deduced from the different experiments in which the conditions were similar, differed considerably, occasionally by as much as 1 per cent. The cause was evident: the depth of liquid was too small to give satisfactory results with this form of stirrer. Considerable difficulty was experienced in maintaining the potential balance, and it is possible that at times portions of the coils were uncovered. I therefore decided on increasing the depth of the liquid.

*Experiments* 6 *to* 8.—The mass of aniline was now increased by about 60 grms., and the observations became more satisfactory. These experiments were performed with a stirring rate of 9·10 per second. I had not yet decided upon the best method of ascertaining the null point, and unfortunately did not perform any 4-cell experiments. When deducing the results, I assumed that the intersection of the 2- and 3-cell lines stood in the same relative position to the intersection of the 2- and 4-cell lines as was found in those cases where a 4-cell experiment had been performed.

The null point is of course (see Plate VIII.) in a very different position from that found when the stirring-rate was 5·00 ; and the close agreement between the results given by these three experiments at the high rate, and experiments 13 to 15 at the same temperature but with a slow rate, is a satisfactory proof of the validity of this method of finding $\theta_N$.

*Experiments* 8 *to* 39 call for no special comment. They were all conducted with a stirring-rate of (approximately) 5·00; Nos. 9 to 24 with the same mass of aniline as 6 to 8. From No. 25 upwards the mass of aniline was increased to 569·53 grms.

On plotting the values of the capacity for heat of this mass of aniline and the calorimeter, the spot obtained from experiments 25 to 27 appeared in a somewhat abnormal position ; consequently, although I had considered the experimental work as completed, I decided to repeat these experiments, and Nos. 40, 41, and 42 give the result. They agree so closely with the corresponding group as to confirm the position originally assigned to the curve at that temperature (about 16°·7 C.).

The curves on Plate IX. (A) give the capacity for heat of the different masses of aniline together with the calorimeter, at different temperatures. Both of the curves resulting from the larger masses show a marked change between 15° and 25° C. It is worthy of notice that the specific heat as deduced from these curves shows little or no signs of any similar change, but that it appears very markedly in the water-equivalent curve, and in such a manner as to indicate that it was approaching a minimum. Had I not been able to determine the specific heats by methods independent of the behaviour of the calorimeter, I should have concluded that the temperature coefficient of the specific heat of aniline altered considerably at the lower temperatures.

This indicates the necessity for extreme caution in similar investigations.

Chart A.

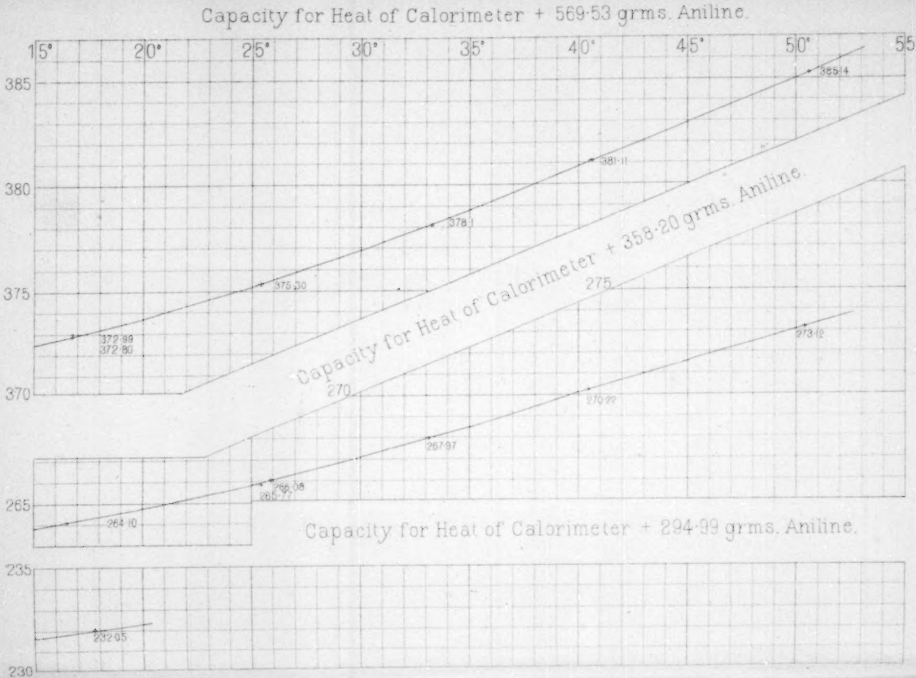
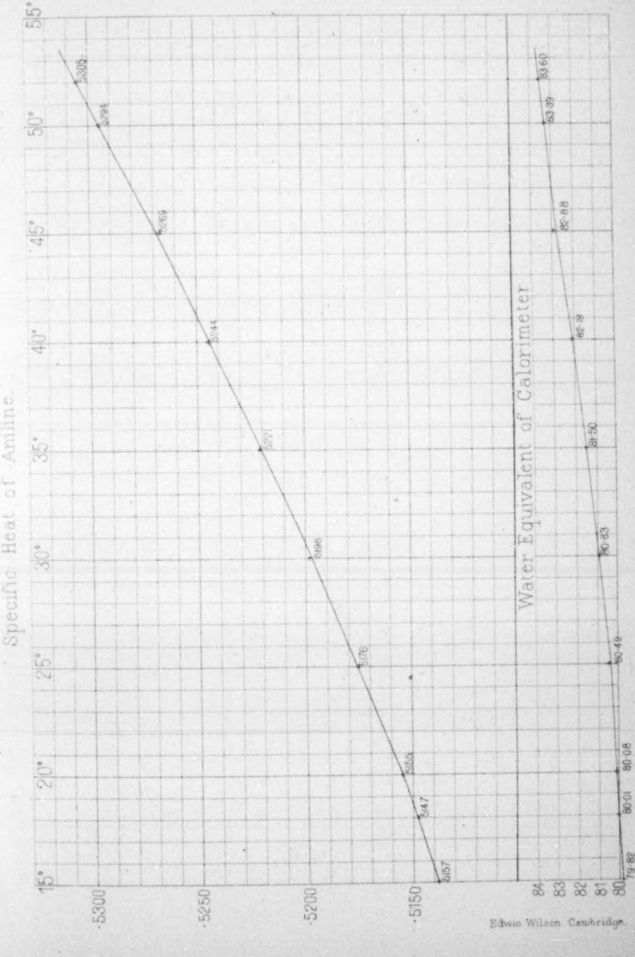

Capacity for Heat of Calorimeter + 569·53 grms. Aniline.
Capacity for Heat of Calorimeter + 358·20 grms. Aniline.
Capacity for Heat of Calorimeter + 294·99 grms. Aniline.
15°
20°
25°
30°
35°
40°
45°
50°
55°
385
380
375
370
275
270
265
235
230
372·99
372·80
375·30
378·1
381·11
385·14
264·10
265·77
266·08
267·97
270·22
273·12
232·05

Chart B.



Edwin Wilson. Cambridge.

Table VI. gives a summary of the results, obtained from the values given by the curves in Plate IX. (A).

## TABLE VI.

Col. I. gives the capacity for heat of calorimeter +358·20 grms. (*in vacuo*) of aniline.
„ II. gives the capacity for heat of calorimeter +569·53 grms. (*in vacuo*) of aniline.
„ III. is the difference between the numbers in Cols. I. & II., and is therefore the capacity for heat of 211·33 grms. (*in vacuo*) of aniline.
„ IV. the specific heat of aniline at the respective temperatures.
„ V. the water-equivalent of the calorimeter.

| Temp. $\theta_1$. | I. | II. | III. | IV. | V. |
|---|---|---|---|---|---|
| | $S_1M_1+w_1$. $M_1=358\cdot20$. | $S_1M_2+w_1$. $M_2=569\cdot53$. | $S_1(M_1-M_2)$. $M_1-M_2=211\cdot33$. | $S_1$. | $w_1$. |
| 15° | 263·82 | 372·38 | 108·56 | ·5137 | 79·82 |
| 18 | 264·36 | 373·13 | 108·77 | ·5147 | 80·02 |
| 20 | 264·74 | 373·69 | 108·95 | ·5155 | 80·11 |
| 25 | 265·80 | 375·14 | 109·34 | ·5175 | 80·44 |
| 30 | 267·10 | 376·88 | 109·86 | ·5198 | 80·90 |
| 35 | 268·50 | 378·82 | 110·32 | ·5221 | 81·49 |
| 40 | 270·02 | 380·86 | 110·84 | ·5244 | 82·19 |
| 45 | 271·58 | 382·90 | 111·32 | ·5268 | 82·88 |
| 50 | 273·00 | 384·88 | 111·88 | ·5294 | 83·39 |
| 52 | 273·55 | 385·63 | 112·08 | ·5304 | 83·60 |

Experiments 1 to 5 give $\frac{T}{J}=232\cdot05$ (Table V. *supra*) when $M_3=294\cdot99$, and $\theta_1=17^{\circ}\cdot78$ C. From the above table we get $w_1=80\cdot01$ when $\theta_1=17^{\circ}\cdot78$.

Hence

$$S_1M_3+w_1=232\cdot05$$
$$w_1=\phantom{2}80\cdot01$$

$$\therefore\ S_1M_3=152\cdot04 \quad \text{hence } S_1=\underline{\cdot5154}$$ (*cf.* with ·5146 *supra*).

Again, the early experiments with water (p. 245) gave :—

when $\theta_1=17\cdot2$ $w_1=80\cdot1$
and $\theta_1=17\cdot2$ $w_1=79\cdot8$

hence when $\theta_1=17\cdot2$ $w_1=\underline{79\cdot95}$ (*cf.* with 79·99 *supra*).

Although I have referred to experiments 1 to 5 as unsatisfactory in themselves, the value obtained from them is (as above pointed out) in fair agreement with that deduced from the remaining experiments.

The same remark applies to the absolutely independent determinations of the water-equivalent when conducted with water itself, and they afford strong corroborative testimony as to the accuracy of the conclusions.

The following simple formula gives the specific-heat curve with sufficient accuracy:—

$$S_1 = 0{\cdot}5156 + (\theta_1 - 20) \times {\cdot}0004 + (\theta_1 - 20)^2 \times {\cdot}000002. \quad \text{(A)}$$

The following table gives the experimental results and those obtained from the above formula.

TABLE VII.

| $\theta_1$. | $S_1$ (Experimental Results). | $S_1$ (from formula A). |
|---|---|---|
| 15° | ·5137 | ·5137 |
| 20 | ·5155 | ·5156 |
| 25 | ·5175 | ·5176 |
| 30 | ·5198 | ·5198 |
| 35 | ·5221 | ·5221 |
| 40 | ·5244 | ·5244 |
| 45 | ·5268 | ·5269 |
| 50 | ·5294 | ·5294 |
| 52 | ·5304 | ·5305 |

I have made a careful search for records of previous determinations, but I have been unable to find any in addition to those given in Landolt and Börnstein's tables—which are as follows:—

| Temp. | $S_1$. | Observer. |
|---|---|---|
| 8° to 82° | ·5120 | Schiff. |
| 12° to 138° | ·5231 | ,, |
| 12° to 150° | ·464 | Petit. |

NOTE (*Sept.* 6, 1894).—Having unfortunately strained one of the leads when the tank was at a high temperature, the insulation between the coil and the steel chamber commenced to fall off on Sept. 1st. I have therefore most reluctantly been compelled to take the whole apparatus to pieces, in order to replace the ebonite insulators. On Sept. 3rd I withdrew the whole of the aniline, and on examining it I found that in colour it had darkened considerably. The experiments described in this paper were completed on Aug. 3rd, and on Aug. 16th the apparatus was again set going, and was kept continually at work until Sept. 3rd. During this time electrical currents were continually passing through the coil and the stirrer must have made some millions of revolutions. The nature of the experiments that I was then engaged upon compelled close attention to the capacity for heat of the aniline, and I am convinced that even a small change in the specific heat could not have escaped my notice. It would appear, therefore, that the change indicated by this darkening was not of a nature to sensibly affect the specific heat.

NOTE, *Dec.* 7, 1894.—In a communication made to the Royal Society on November 22, Professor Schuster pointed out an error in my determination of the value of J, viz. that I had not made a necessary correction for the specific heat of the air displaced by the water; for the method I had adopted gave the difference in the rate of rise when a certain space was filled first with air and then with water. This correction raises my value of J by about 1 in 4000.

Now the specific gravity of aniline (1·02) but slightly exceeds that of water; and as the method described in the preceding pages also depends upon the measurement of differences in the rate of rise, the correction would eliminate and would, therefore, not affect the values of the specific heat of aniline as given in Table VII. Again, if there are any errors in the values of the electrical standards upon which my determination of J depends, they also would eliminate during the calculations by which the specific heat of aniline was ascertained. There can, therefore, be no doubt that the value assumed for J ($4{\cdot}198 \times 10^7$) is the correct one to be used for the reduction of the observations on aniline.

## DISCUSSION.

Dr. ARMSTRONG thought the author had made a particularly happy selection in aniline, for it could now be obtained in almost any quantity absolutely pure. When pure it did not discolour on exposure, and would probably be very satisfactory as a standard liquid. He doubted whether any hydrocarbon could be better.

Prof. **Ayrton** congratulated the author on the extreme accuracy obtained. Recently he had arranged an experiment to determine the mechanical equivalent of heat by the electrical method, which gave very accurate results, without any corrections whatever being necessary.

Prof. S. P. **Thompson** thought the whole phraseology of specific heat required revising.

Prof. **Perry** agreed with Mr. Griffiths that a name for "capacity for heat per unit volume" was greatly needed, and Mr. Lucas suggested "heat density," but this was not satisfactory.

Dr. **Sumpner** said most text-books on physics attributed the advantage of the mercury thermometer to the low specific heat of mercury, whereas the capacity for heat per unit volume was the important factor.

Mr. **Watson** enquired to what temperature the alloy which the author had used to connect glass to metal had been tested?

The **President** said the paper was of great importance, because it dealt with the application of electrical methods to thermometry. The mercury thermometer had been quite superseded for work such as had just been described.

Mr. **Griffiths**, in reply to Mr. Watson, said the alloy had been used successfully between 10° and 62° C. It gave way at 71° C. He was glad to learn from Dr. Armstrong that aniline could now be got pure. Prof. Ramsay had written to say that he did not think that the slight impurities in ordinary aniline would have much effect on its specific heats.

Mr. **Blakesley** asked if aniline could be taken as pure if it did not change colour on exposure.

Dr. **Armstrong**, in reply, said, Yes ; if the boiling-point was also constant.

# XXV. *The Influence of the Relative Volumes of Liquid and Vapour on the Vapour-Pressure of a Liquid at Constant Temperature.* *By* SYDNEY YOUNG, *D.Sc., F.R.S., University College, Bristol*[*].

THE question whether the vapour-pressure of a liquid at a given temperature depends on the relative volumes of liquid and vapour has been frequently discussed, and has been the subject of many experimental investigations. Within recent years extended researches on the relations between the temperatures, pressures, and volumes of several liquids have been carried out by Prof. Battelli, and he arrives at the conclusion that when, in a tube containing a perfectly pure liquid and its vapour, the volume is diminished and the vapour caused to condense, the vapour-pressure rises: in other words, that the smaller the relative volume of vapour the higher is the vapour-pressure.

These results are entirely opposed to those obtained by Dr. Ramsay and myself and, while referring to this question in a letter to the 'Philosophical Magazine' last February, we ventured to characterize the conclusions of Prof. Battelli as incorrect, and to suggest that the error was due to the presence of small quantities of air or other impurity in the liquid examined and to the employment of insufficiently purified substances for heating-purposes.

In a letter published in the August number of the 'Philosophical Magazine' Prof. Battelli adheres to the conclusion previously stated, and does not admit the existence of either of the sources of error suggested. "I would rather observe," he writes, "that, in order to observe such a phenomenon, an apparatus is necessary which enables us—as in my case—slowly to compress the vapour, and to maintain it for a time under constant pressure."

There can be no doubt, I think, that such an apparatus is required in order to decide *the question whether the phenomenon exists*, but it seems hardly necessary to point out that the conditions described are fulfilled in the apparatus employed by Dr. Ramsay and myself.

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[*] Read November 9, 1894.

During the present year I have been engaged in an investigation of the thermal properties of isopentane—a liquid, boiling at 28°, which can, by suitable treatment, be obtained in a pure state *.

A great number of determinations of the vapour-pressure of the liquid were made at various temperatures, and in many cases the volumes of liquid and vapour were read. The results obtained prove conclusively that the vapour-pressures of isopentane are independent of the relative volumes of liquid and vapour; and it may be of interest to give all the observed vapour-pressures at two temperatures, with the corresponding volumes of vapour and liquid.

The same apparatus was employed as in my previous work on benzene and its derivatives, the esters, &c.: it is similar in principle though it differs somewhat in detail from that made use of by Ramsay and myself (Phil. Trans. 1887 A, p. 59).

The tube containing the isopentane was heated by the vapour from pure liquids (Trans. Chem. Soc. 1885, p. 640; 1889, p. 483) boiling under reduced pressure.

The pressures are corrected for (1) the difference in height of the columns of mercury in the tube containing the isopentane and in the air-gauge; (2) the expansion of the heated column of mercury; (3) the pressure of the column of isopentane; (4) the deviation of air (in the air-gauge) from Boyle's law, as determined by Amagat.

Several series of determinations were made with different quantities of liquid in the tube. As a rule four readings of pressure were taken in each series at each temperature.

It will be seen that although the relative volumes of vapour and liquid vary within very wide limits, there is no such corresponding variation in the vapour-pressures, the greatest difference from the mean value at 140° being slightly less than 0·1 per cent., and at 90° slightly greater—in no case outside the limit of experimental error.

It has happened occasionally in the course of this or previous investigations that a trace of air has entered the tube

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* Full details of the method of purification adopted will be described later when the research is completed.

Temperature =90°.

| Series. | Volume of Vapour in c.c.'s. | Volume of Liquid in c.c.'s. | Ratio $\left\{\frac{\text{Volume of Vapour.}}{\text{Volume of Liquid.}}\right.$ | Vapour-Pressure. | Difference from Mean. |
|---|---|---|---|---|---|
| II. | 0·016 | 0·52 | 0·03 | 4280 | −1 |
| III. | 0·025 | 0·20 | 0·12 | 4281 | 0 |
| II. | 0·105 | 0·52 | 0·20 | 4286 | +5 |
| I. | 0·07 | 0·23 | 0·30 | 4281 | 0 |
| „ | 0·17 | 0·23 | 0·74 | 4280 | −1 |
| III. | 0·17 | 0·19 | 0·89 | 4279 | −2 |
| I. | 0·28 | 0·23 | 1·2 | 4281 | 0 |
| III. | 0·30 | 0·19 | 1·6 | 4277 | −4 |
| I. | 0·38 | 0·23 | 1·7 | 4282 | +1 |
| III. | 0·42 | 0·19 | 2·2 | 4281 | 0 |
| Temperature =140°. | | | | | |
| II. | 0·012 | 0·54 | 0·02 | 11636 | −2 |
| „ | 0·06 | 0·54 | 0·11 | 11634 | −4 |
| III. | 0·06 | 0·20 | 0·30 | 11643 | +5 |
| I. | 0·08 | 0·24 | 0·33 | 11637 | −1 |
| IV. | 0·06 | 0·07 | 0·86 | 11638 | 0 |
| I. | 0·20 | 0·23 | 0·87 | 11636 | −2 |
| III. | 0·20 | 0·18 | 1·11 | 11643 | +5 |
| V. | 0·07 | 0·06 | 1·2 | 11634 | −4 |
| I. | 0·32 | 0·21 | 1·5 | 11641 | +3 |
| III. | 0·34 | 0·17 | 2·0 | 11649 | +11 |
| I. | 0·43 | 0·20 | 2·2 | 11642 | +4 |
| III. | 0·48 | 0·16 | 3·0 | 11647 | +9 |
| IV. | 0·23 | 0·05 | 4·6 | 11633 | −5 |
| V. | 0·26 | 0·04 | 6·5 | 11635 | −3 |
| IV. | 0·39 | 0·03 | 13·0 | 11632 | −6 |
| V. | 0·45 | 0·02 | 22·5 | 11636 | −2 |
| IV. | 0·56 | 0·02 | 28·0 | 11634 | −4 |
| V. | 0·62 | 0·002 | 310·0 | 11632 | −6 |

or has been left in the liquid, and in a very few cases (ethyl formate, propyl formate) a small quantity of permanent gas has been formed by partial decomposition of the liquid by prolonged heating at high temperatures. The presence of permanent gas (or of very volatile impurity) is clearly indicated by the increase of pressure required for the complete condensation of the vapour, and the following points have been noticed in such cases:—(1) The pressure does rise as the volume of vapour diminishes; (2) the readings taken with diminishing volumes are higher than with increasing volumes. This may be readily explained; for when the whole of the substance is in the state of vapour the air is diffused uniformly through it, and when condensation is brought about by compression the air remains to a large extent in the vapour above the liquid and dissolves but slowly in the liquid formed consequently, as the volume of vapour diminishes the undissolved air becomes more and more compressed, and its pressure increases and becomes considerable when the vapour is nearly all condensed. Similarly, with an impurity more volatile than the pure substance, a partial "fractionation" of the liquid takes place, the less volatile pure substance condensing first, whilst the vapour becomes more and more contaminated with the more volatile impurity.

On the other hand, when the readings are taken with increasing volume, the air or volatile impurity is at first uniformly distributed through the liquid, and it escapes but slowly through the long column of liquid into the vapour above. Thus when a reading is taken with a relatively small volume of vapour, the air present has a much greater influence in the first case than the second, but when the volume of vapour is relatively large its influence is small in both cases. I have noticed repeatedly that the freer a liquid is from air or permanent gas, the more closely do the readings during compression and expansion agree.

The presence of a small quantity of impurity less volatile than the pure substance may escape detection so long as the volume of liquid, relatively to that of the vapour, is fairly large; but its influence becomes very marked when the quantity of liquid is relatively very small. Thus, on one occasion, the isopentane had come in contact for a moment with an indiarubber tube and had, no doubt, dissolved a minute quantity of it. It was noticed in this case that the mercury was slightly tarnished (owing in all probability to the sulphur in the indiarubber), but the vapour-pressures, when there was plenty of liquid present, agreed among themselves and with previous determinations. When, however, the volume was increased until nearly the whole of the liquid was evaporated, the observed vapour-pressures were far too low, and diminished rapidly as the volume was increased.

In this case and in those in which the presence of any permanent gas was detected, the experimental results were rejected and the tube was refilled.

## DISCUSSION.

The CHAIRMAN remarked that, although the *à priori* considerations against Prof. Battelli's view were very great, it was satisfactory to have had the experimental enquiry carried out with such care and accuracy by Dr. Young.

## XXVI. *The Significance of Wiener's Localization of the Photographic Action of Stationary Light-Waves. By* J. LARMOR, *F.R.S., Fellow of St. John's College, Cambridge*[*].

THE experiments by which Wiener demonstrated[†] that, when stationary plane-polarized optical undulations are produced in a photographic film, by reflexion of a stream of incident plane-polarized light at a metallic or other backing, the photographic action occurs at the antinodes of Fresnel's vibration-vector and not at the nodes, have been employed by its author and others to decide between the various theories of light. If for purposes of precise description we utilize the terminology of the electric theory of light, which formally includes all the other theories by proper choice of the vibration-vector, we may say that the photographic action takes place at the antinodes of the electric vector which corresponds

[*] Read November 9, 1894.

[†] Wiedemann's *Annalen*, 1890.

to Fresnel's vibration, and not at the intermediate antinodes of the magnetic vector which corresponds to MacCullagh's and to Neumann's vibration.

The crucial experiment of Wiener relates to the case when the angle of incidence is half a right angle, so that the direct and reflected waves which interfere are at right angles to each other. If the vibration take place along the direction of intersection of the two wave-planes, it will present a series of nodes and antinodes ; but if in the perpendicular direction there will not be such alternations of intensity. The experiment showed that when the light is polarized in the plane of incidence, the photographic plate develops a series of bands ; but when it is polarized in the perpendicular plane these bands are absent.

The argument employed is that the photographic effect will be greatest at those places in the stationary wave-train where the vibration is most intense ; and the conclusion is drawn from it that the actual vibration is represented by Fresnel's vector and not by MacCullagh's ; in other words, that the vibrations of polarized light are at right angles to the plane of polarization. The force of this argument, as against MacCullagh's theory, would, however, be evaded if the vector of that theory were taken to represent something different from the linear displacement of the æther, or if vibrations were excited in the molecule by rotation instead of translation, or by stress, as Poincaré has pointed out *.

But as a matter of fact it seems difficult to assign any reason of the above simple kind, on either theory, in favour of the photographic disturbance occurring at the antinodes rather than at the nodes of the optical vibration. The remarkable suggestion thrown out by Lord Rayleigh some time previous to Wiener's experiments, and afterwards verified by Lippmann, that certain effects in colour photography produced by Fox Talbot and Becquerel were really due to this kind of localization of the photographic effect, is not in opposition to such a view ; for the consideration adduced was simply that a localization, periodic with the waves, would, if it happened to exist, produce effects like the observed ones. At any rate,

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* See a discussion on this subject in *Comptes Rendus*, cxii. 1891, in which MM. Cornu, Poincaré, and Potier took part.

the observed localization demonstrates the important result that the effect is due to a specific dynamical action of the waves, and not to mere general absorption of the radiation.

Let us consider the actual circumstances of the case. There are about $10^3$ molecules of the sensitive medium in the length of a single wave of light: thus in the stationary wave-train all the parts of a single molecule would at any instant be moving with a sensibly uniform velocity, which increases and diminishes periodically. The vibration of the molecule would thus be, were it not for the influence of differences of inertia or elasticity between its parts and the surrounding æther, very nearly a swaying to and fro of it as a whole: if it were exactly this, it could not be expected to produce any breaking up of the molecule at all. Moreover, as at the antinodes of the vibration there is movement but no stress in the medium, so at the nodes there is stress but no movement; and it does not seem at all clear that alternating stress might not be as potent a factor in disintegration as alternating motion. A representation has been constructed by Lord Kelvin [*] of a system in which internal vibrations can be excited by simple translation, by means of the device of an outer shell imbedded in the æther and containing inside it masses with spring connexions; and such a system might also be adjusted so as to respond to simple rotation, and therefore be excited at the nodes of the wave-train instead of the antinodes.

A theory based in this manner on difference of inertia must take the density of the æther to be very minute compared with that of matter; therefore if the molecule is to have free periods of the same order of magnitude as the periods of the incident light-waves, the elastic forces acting between the atoms and concerned in these periods must be very intense. But Lord Kelvin's well-known estimate of the rigidity of the æther on this hypothesis makes it very small compared with the ordinary rigidity of material bodies [†]. In fact on Pouillet's data, which imply a considerable underestimate, the energy of the solar radiation near the sun's surface is about $4 \times 10^{-5}$ ergs per cubic centimetre; it easily follows that if the amplitude of the æthereal disturbance is, say, $\epsilon$ times the wave-length, the density of the æther must be about $1/10^{22}\epsilon$, and its rigidity, which is equal to the density multiplied by the square of the velocity of propagation, therefore $1/10\,\epsilon^2$. On an elastic solid theory it is desirable to have the density very small: thus if we adopt $10^{-2}$ as the maximum likely value of $\epsilon$, the density of the æther comes out $10^{-18}$ of that of water, and its rigidity about $10^3$, whereas the rigidity of steel or glass is of the order $10^{11}$.

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[*] "Lectures on Molecular Dynamics," Baltimore, 1884.

[†] *Cf.* Maxwell, *Encyc. Brit.*, article "Æther."

Now at first sight it would appear that the elastic tractions exerted by an æther of such small rigidity on an imbedded molecule swaying backwards and forwards in it, would be vanishingly small compared with the elastic forces between its constituent atoms which are concerned with free vibrations of the kind of period under consideration; and that therefore they would be quite incompetent to produce violent disturbance in the molecule. But on a closer examination this difficulty may to a considerable extent be evaded.

Let us imagine an imbedded rigid nodule of linear dimension L, and let the force necessary to displace it in the æther in any manner through a distance $x$ be L$x$. Let us compare with it a similar nodule of linear dimensions $\kappa$L displaced through a distance $\kappa x$. There is complete dynamical similarity between the two cases; the strains at corresponding points in the æther are equal, and therefore so are the tractions per unit area. Thus the forcive necessary in the latter case to produce the displacement $\kappa x$ is $\kappa^2$L$x$, and therefore to produce the same displacement $x$ as in the previous case a forcive $\kappa$L$x$ is required. If now instead of comparing the total forcives in the two cases we compare the forcives per unit volume, an increase of linear dimensions in the ratio of $\kappa$ to one diminishes this forcive in the ratio of $\kappa^2$ to one. Thus, if only the atoms are taken small enough, an æther of very slight rigidity can exert a forcive on them which, estimated per unit volume, is of any order of magnitude we please. The features of the case are in fact analogous to those of the suspension of small bodies, such as motes, in a viscous fluid medium like the atmosphere: if only the particles are small enough they will float for an indefinitely great time against the force of gravity, even be they as dense as platinum,—the only limit being in that case the one imposed by the molecular discreteness of the air itself.

It would appear that the application of this principle does much to vivify the notion of an elastic solid æther. A medium of this kind, which is excessively rare and, as a consequence, of very feeble elasticity, would exert practically negligible tractions on the surfaces of a mass of matter in bulk, while it may exert relatively very powerful ones on the individual atoms of which the mass is composed if only they are sufficiently small, it being of course supposed that the structure of the medium itself is absolutely continuous. And it would even appear that a medium of very small density and rigidity may be competent to excite powerful vibrations in the molecules notwithstanding the strength of the forcives which hold them together.

We may thus imagine a working illustration of a ponderable transparent medium of elastic solid type as made up of very small spherical nodules of great density and rigidity dispersed through the æther and imbedded in it. We may even imagine these nodules to be collected into more or less independent groups, each of which will have free periods of relative vibrations of its own nearly independent of other groups, in the manner now well known in connexion with Prof. Ewing's model of a magnetic medium. A wave running across such a medium may excite these groups, and thus illustrate the theory of selective absorption by means of a system in which only the elasticity of the ambient medium is operative, but no other internal forcive.

The explanation of a very weak medium exciting such powerful tractions implies of course strains of enormous intensity, so that its limits of perfect elasticity must be taken enormously wide compared with anything we know in ordinary matter. The magnitude of the strains also requires that the displacement of an atom relative to the æther must be a considerable fraction of its diameter; and this is sufficiently secured by the large value of $\epsilon$ above that which is required to keep down the density of the æther, combined with the great relative density of the atom. It would thus seem to be possible to account for sufficiently large differential tractions between the component atoms of a molecule, especially if some of them lie well under the lee of others, to produce brisk internal vibration.

In this way we could imagine the construction of a sort of model illustrative of an elastic solid theory of refraction, including selective absorption and other such phenomena, in the form in which it is presented by von Helmholtz and others. In the simpler case, in which the atoms are not grouped into systems capable of synchronous free internal vibrations, let $(\xi, \eta, \zeta)$ denote the mean displacement of the free æther, and $(\xi_1, \eta_1, \zeta_1)$ that of the atoms. Then the equations of vibration assume the forms

$$\rho \frac{d^2}{dt^2}(\xi, \eta, \zeta) = c\nabla^2(\xi, \eta, \zeta) - \left(\frac{d}{dx}, \frac{d}{dy}, \frac{d}{dz}\right)p + a(\xi_1 - \xi, \eta_1 - \eta, \zeta_1 - \zeta),$$

$$\rho_1 \frac{d^2}{dt^2}(\xi_1, \eta_1, \zeta_1) = -a(\xi_1 - \xi, \eta_1 - \eta, \zeta_1 - \zeta)^*,$$

in which $p = c'\left(\frac{d\xi}{dx} + \frac{d\eta}{dy} + \frac{d\zeta}{dz}\right)$; and the phenomena of crystalline media could be included by assuming a vector-coefficient instead of the scalar $a$.

The conclusion, then, is that in this limited range an elastic-solid theory of a very rare æther is not so much at fault as would at first sight appear.

A theory based on difference of rigidity without difference of inertia, after MacCullagh's manner, would have to be realized by ascribing to the atom an atmosphere of intrinsic æthereal strain, instead of endowing it with great inertia; and this could only be possible in a rotational æther, and would in fact form a mechanical representation of the electric theory. As such it must be expected to give an account of the phenomena of electricity as well as those of light[*], and in such an account is founded one of its chief claims.

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* There are introduced by von Helmholtz (*Wiss. Abh.* ii. p. 216) in addition, a forcive proportional to the absolute displacement of the atom, and a frictional one proportional to its absolute velocity. The former is derived from the idea that the heavy central masses of the atoms are unmoved by the æther, and only outlying satellites are affected by its motion. On our present view this restriction might be dispensed with, except in so far as it renders possible an illustrative theory of absorption of an analytically simple character. The consequences of the above equations are set out by various writers, *e. g.* Carvallo (*Comptes Rendus*, cxii. p. 522).

A development of the electric theory has recently been essayed by von Helmholtz[†], on the basis of the formal equations of Heaviside and Hertz, in which the free æther is still supposed to be an elastic medium of excessively small density in which the dense atoms are imbedded. If such a view should turn out to be the basis of a consistent body of theory, the considerations given above with respect to the intensities of molecular tractions would have a bearing on it also.

Let us now consider more particularly the explanation that would be offered by the electric theory of light. The difference between a material medium and a vacuum consists in an altered effective dielectric coefficient. This difference is simply and naturally explained by the hypothesis that the material molecules are polar owing to their associated atoms having atomic charges equal in amount but opposite in sign, and that they therefore possess electric moments just as the molecules of a magnet possess magnetic moments. An electric force thus tends to pull the two constituents of a molecule asunder; and its full intensity is exerted in this manner, not merely its differential intensity over the range of the molecular volume. But a magnetic force has no such tendency even when we take the molecule to be magnetically polarized, because the two poles of a magnetic element cannot be dissociated from each other; the magnetic moment is thus directly associated with the atom, not with the molecule. In the case of the stationary light-waves the antinodes of the electric force are therefore places where alternating disturbances of a kind suitable to produce decomposition of the molecules are maintained, and may produce strong effects through sympathetic molecular vibration or otherwise; but at the intermediate antinodes of the magnetic force the individual ultimate atoms may be disturbed by the alternating magnetic force, but there is no tendency to separation of the constituents of the molecule. On the electric theory, therefore, there is abundant justification both for the magnitude of the effect produced, and for its localization as determined by Wiener's experimental investigation.

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[*] *Cf.* "A Dynamical Theory . . . ," Phil. Trans. 1884, §§ 122–124.

[†] Wied. *Ann.* 1894.

The theory, noticed first it seems by Weber, which ascribes molecular magnetism to the orbital rotation round each other of ionic charges, and which has very strong recommendations from the point of view of the dynamics of the æther, may form a partial exception to this statement. It leaves the question open as to whether the principal part of the magnetic moment is due to orbital motions in the atoms or to the motions of the constituent atoms in the molecules; though it suggests strongly the latter alternative. In that case there will usually be a differential magnetic action of the field as between these moving atoms; but the magnetic actions on positive and negative ions will be by no means equal and opposite, as is true of the electric actions. Thus, for example, in the limiting case of two equal and opposite ions revolving round each other, the elements of the equivalent ionic convection-currents will be at each instant parallel, and there will be no differential magnetic forcive at all; there will also be no magnetic moment; but the electric differential action will retain its full force.

It is well understood, and in accordance with this explanation, that the energy of chemical combination of atoms into molecules is almost entirely that of electrostatic attraction of their atomic charges. In fact the electric attraction between them diminishes according to the law of inverse square with increasing distance, their magnetic attraction according to the law of the inverse fourth power: if these forces are of the same order of magnitude in the actual configuration of the atoms in the molecule, the work done by the former during their combination must be almost indefinitely greater than the work done by the latter.

If we contemplate the purely dynamical basis which must underlie the descriptive explanations of the electric theory of light, it is difficult to see how there can be any place for a theory of the æther loaded by the material molecules, which dynamical views usually associated with Fresnel's theory demand. There could be no polarity in the inertia of a mere load, such as the present considerations require. On the other hand, the presence of electrically polarized molecules is effectively a diminution of the elasticity of the luminiferous medium; and I have tried to show elsewhere * that the principles of MacCullagh's theory of optics are in substantial agreement with all the general features of our electrical and optical knowledge.

It is definitely implied in the electromotive, as distinguished from an electrodynamic, character of the electric theory of light, that the atomic charges vibrate in unison with the light-waves, quite unimpeded by any material inertia of their atoms. This hypothesis is conceivable and natural, independently of any particular explanation, on the theory that the atoms are themselves intrinsic mobile configurations of stress or motion, or both together, in the ultimate medium.

[It is not without interest to consider how far the conception mentioned above of an isotropic solid medium of very small density, with very massive minute nodules imbedded in it but exerting no direct forcives on each other, will carry us in forming a representation of optical phenomena. The theory is of the Young-Sellmeier type, because each nodule has one or more free periods conditioned by its form and by the surrounding elasticity.

On eliminating $(\xi_1, \eta_1, \zeta_1)$ from the equations expressed above, we obtain the vibrational equations of the æther, supposed thus loaded. Its elastic properties are found to be conserved intact, but the effective density as regards vibrations of period $\tau$ is increased by $a\rho_1 \Big/ \left(a - \frac{4\pi^2}{\tau_2}\rho_1\right)$. When the coefficient $a$ is of aeolotropic type, by reason either of the form or the distribution of the nodules, we have effectively an isotropically elastic medium with aeolotropic inertia; this leads to Fresnel's wave-surface, provided the elasticity is labile in Lord Kelvin's sense. The theory also leads to a formula for ordinary dispersion, of the usually admitted type (Ketteler's) for isotropic media; but, on the other hand, it is in default by assigning a dispersional origin to double refraction. If we wish to include the minute effect known as the dispersion of the optic axes in crystals, it will be necessary to assume for the elastic stress between æther and matter a

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* *Loc. cit.* Phil. Trans. 1894.

somewhat more general form, involving (after von Helmholtz) absolute as well as relative displacement, but always of course remaining linear.

The assumption of elasticity of labile type also allows an escape from the usual difficulties of a solid æther in the matter of reflexion. In that problem the elasticity would naturally be taken continuous across the interface, the volume occupied by the molecules being on this hypothesis extremely small compared with that occupied by the æther.

We may further amend the theory by getting rid of the difficulties associated with lability, at the same time avoiding the difficulty as to how a body can move through a perfect solid medium, if we take the æther to be a rotationally elastic fluid, and retain the material load as before.

But an essential and fundamental difficulty will still remain. It is the extremely small volume-density of the energy involved in radiation which permits a very small inertia, and consequently a small elasticity, to be assigned to the æther, and so prevents it from acting as an appreciable drag or exerting an appreciable force on finite bodies moving through it. But these very properties would incapacitate it for acquiring the very large volume-densities of energy that would have to be associated with it in order to explain electrodynamic phenomena.

Any representation which would make the æther consist of molecules of ordinary matter is open to the objection that the thermal kinetic energy of gases and other material systems must then, in accordance with Maxwell's law of distribution of energy, largely reside in it. But, on the other hand, if we hold to the view of matter which was first rendered precise by Lord Kelvin's theory of vortex atoms, namely, that the æther is the single existing medium and that atoms of matter are intrinsic singularities of motion or strain which belong to it, then there is no inducement to assume for the æther a molecular structure at all, or to make its inertia anything comparable with the inertia of the atoms on whose play the thermal energy of the movements of the matter consists. On such a theory the inertia, and the resulting kinetic energy, of the matter may be hard to explain, but it is certainly something different from the inertia of the underlying medium in which the atom is merely a form of strain or motion. On such a theory refraction, and also double refraction, will be caused by the atmosphere of intrinsic strain which represents the electric charge on the atom ; and only dispersion will be assigned to the influence of sympathetic vibrations in the atoms or molecules, thus doing away with any difficulty of the kind mentioned above.

In the theory of gases the ordinary kinetic energy of the molecules represents sensible heat, and as such may be derived for example from the dissipation by friction or otherwise of the mechanical energy of ordinary masses : it is of the nature of kinetic energy of the masses of the atoms. But the store of energy which keeps up radiation is of electromotive kind, is concerned with displacing electricity, not with moving matter except indirectly ; at least no consistent scheme has yet been forthcoming which includes both. It is quite conceivable that the disturbances which occur in the ordinary encounters of molecules are of far too gentle a character to excite the very powerful elasticity which on a certain form of the electric theory binds together the continuous medium taking part in optical propagation, any more than a system of solid balls rushing about in an enclosure bounded by a heavy continuous rigid solid can excite sensibly the elastic qualities of that body. The opinion has been widely supported, both on theoretical and experimental grounds, that a gas will not emit its definite radiations however high the temperature to which it is raised, unless there is chemical decomposition of the molecules going on. If that be so, the æther does not act as an equalizer of the kinetic energy between the different modes of vibration of the molecules, and the ordinary theory of gases need make no reference to the æther.

If I have understood aright, a similar view has been expressed as at any rate a possible explanation of the difficulty as to the application of Maxwell's distribution theorem in the theory of gases, by Prof. Boltzmann himself. The law of distribution of energy is perhaps unassailable for the case of molecules like small spheres, with three degrees of freedom, all translational. By including the rotational modes of freedom, which may be none at all for a monad gas, only two for a diad, and three for other types, and these possibly not complete, a sufficient number of freedoms is obtained to cover the known range of values of the ratio of the specific heats. The introduction of any vibrational types would make too many ; so on this ground also it is not likely that such types can enter into those among which the thermal energy is divided.—*December* 4.]

## DISCUSSION.

A letter was read from Professor LODGE, criticising the manner in which Wiener's results had been summarized by Dr. Larmor, the summary at the commencement of the paper being characterized as misleading. The letter concluded with an expression of admiration for the work done by Dr. Larmor in working out electricity and optics, starting from McCullagh's theory of light.

Dr. STONEY objected to the suggestion that atomic charges could vibrate unimpeded by material inertia. We had not merely to consider the bodily translation of a molecule, but the relative motion of its parts. Radiation absorbed by a gas acted on its atomic charges,—part appearing as translational energy of the molecules, part as energy of their internal motion, and the ether acting as an equaliser of molecular energy.

Prof. MINCHIN did not understand why the polarised light in Wiener's crucial experiment should be incident at 45°. He also found it hard to imagine what vector other than the simple displacement of the ether could be the vector of McCullagh's theory.

Dr. BURTON said he found no difficulty in following Dr. Larmor's statement of Wiener's results ; it appeared to him perfectly clear and satisfactory.

# XXVII. *On a Suggestion by* Professor J. J. Thomson *in Connexion with the Luminescence of Glass due to Kathode-Rays.*

*By* John Burke, *B.A., Lecturer in Physics, Mason College, Birmingham.*[*]

Last August, at Oxford, I communicated a paper to the British Association on a strange luminous phenomenon which had been observed by Beccaria more than a hundred years ago. It was there pointed out that although the conclusions arrived at by the Italian physicist, if true, were likely to lead to results of an extremely interesting character, in connexion with Mr. Crookes' important researches on the luminescence of glass, &c., in vacuum-tubes, and although the mysterious nature of the phenomenon was likely to attract much attention, yet the subject was allowed to retain its obscurity. Beccaria ('Artificial Electricity,' § 766) observed that when *vacuum*-bulbs were broken in the dark a light, consisting of a faint glow, was produced in the place where the bulb lay. He attributed an electrical origin to the phenomenon, owing to the manner in which certain substances were supposed to behave in yielding the glow. He mentioned, moreover, that the mere breaking of glass did not give rise to the phenomenon, but that the presence of air was essential to its production, and that when air was allowed to rush suddenly into a vacuum by the bursting of a bladder at the mouth of a receiver, articles such as glass bottles, vessels of sealing-wax, &c., became luminous by, he supposed, the violent dashing of the external air on them; the luminosity was most conspicuous at the necks of the bottles or at the upper edges of the vessels

As has already been remarked, Beccaria's researches appear to have been forgotten for more than a century, and not until quite recently has attention been drawn to them. This has been done by Professor J. J. Thomson, who, in his 'Recent Researches in Electricity and Magnetism,' p. 119, recalls the fact and indicates its possible close relationship to Mr. Crookes' theory of the luminescence of the glass in Geissler's tubes :

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[*] Read November 9, 1894.

that the bombardment of the glass by the particles of gas projected from the kathode is intense enough to cause the glass to become luminous. Prof. Thomson quotes from Priestley's 'History of Electricity':—

> "Signor Beccaria observed that hollow glass vessels, of a certain thinness, exhausted of air, gave a light when they were broken in the dark. By a beautiful series of experiments, he found, at length, that the luminous appearance was not occasioned by the breaking of the glass but by the dashing of the external air against the inside when they were broke. He covered one of those exhausted vessels with a receiver, and letting the air suddenly on the outside of it observed the very same light."

That the light observed in both cases was the same, unless the exhausted vessel, which had been covered by the receiver, was broken by the dashing of the external air against it, is a circumstance which, from considerations that shall presently be adduced, I think we may be justified in questioning.

Through the kindness of Prof. FitzGerald in extending to me the facilities afforded in the Physical Laboratory of Trinity College, Dublin, I have been enabled to experiment upon this subject. It would be impossible for me to attempt to render in detail the acknowledgment of what has been due to his invaluable advice and suggestions.

It must be mentioned at the outset that the present investigation has by no means been completed, yet, thus far, it appears that some of Beccaria's results have not been wholly of that degree of exactness which we should have hoped for. It must, however, be borne in mind that scientific appliances in his time were less perfect than they are to-day, and such imperfection may account for much inaccuracy.

A number of incandescent lamps of various sizes with broken filaments were procured. An observer who had been fifteen or twenty minutes in the dark, whose sight had become sufficiently sensitive to the faintest light, broke one of the larger of these bulbs with a hammer, at the same time protecting his face by a plate of thick glass. A faint *white* glow, which lasted but for a very small fraction of a second, was seen in the place where it was known the bulb had lain. The experiment was repeated in the presence of several persons, who testified to the same effect. The intensity of the light seemed to depend upon the size of the bulb—the larger bulbs, about 7 or 8 centim. in diameter, giving a greater intensity than the smaller ones; whilst with bulbs of not more than 2 centim. diameter no luminous effect was perceived.

A circular plate of glass, about 7 centim. in diameter and 2 millim. thickness, was then placed on the mouth of a receiver, the opening of which was about 5 centim. in diameter, and the contact made air-tight, whilst the air in the receiver was exhausted until a vacuum of about 20 millim. had been obtained.

The plate of glass was then broken with a hammer. A beautiful stream of white light was visible throughout the whole receiver. The light, which lasted for a small fraction of a second, resembled that produced when vacuum-bulbs were broken, though it was more distinct, and consisted not merely of a uniform glow, as in that case, but was marked, in addition, by a number of luminous spots of various sizes: in fact the effect presented the appearance of a faint nebula.

On account of the extreme faintness of the light, it was found impossible to photograph it: at least any attempts in this direction have hitherto proved unsatisfactory, even with the most sensitive plates I could procure.

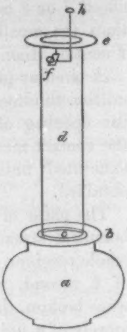
In some instances the luminous spots were observed to be unusually large; the fragments of glass were in such cases also found after each experiment to be of an exceptional size, often 7 or 8 square centim. in area.

This fact is especially worthy of notice, as it undoubtedly indicates that the fragments of glass themselves had become luminous, the continuous glow in all probability having been caused by the very minute fragments.

Different kinds of glass were used without giving any perceptible difference in the effects.

Thin brittle plates of cast-iron and steel were tried in the place of glass, but yielded negative results, owing, perhaps, to the fact that they did not break up into innumerable fragments as glass did readily when struck with a hammer, or because the air was not consequently permitted to enter the vacuum very suddenly and with sufficient violence.

Fig. 1.



Various gases were made to take the place of air. Fig. 1 represents the apparatus employed for this purpose. *a* is a glass receiver; the strong glass ring *b*, the opening of which was covered by a piece of thin glass *c*, rested on the mouth of the receiver *a*, and served to support a long glass tube *d*, at the upper end of which, being closed, there was an arrangement *e* by which a weight *f* was supported and allowed to fall by turning the handle *h* and thus break the glass *c* and open free communication between the gas in the tube *d* and that in the receiver *a*.

The joining between *d* and *a* was made completely air-tight so that no leakage occurred. The tube *d* was then filled with carbon dioxide or oxygen, and the air in the receiver *a* exhausted until a vacuum of about 20 millim. was obtained. The weight *f* was made to fall and break the glass *c*, so that the gas in *d* might enter violently into the vacuum. The same luminous phenomenon was observed as on previous occasions when air was employed, with no perceptible difference as regards colour, intensity, or the general appearance of the glow and luminous spots.

When the gases in both *a* and *d* were exhausted and the glass *c* broken as before, no luminosity whatsoever was observed, thereby showing that the mere breaking of glass did not suffice to produce the phenomenon; but that the presence of a gas was essential, though any gas was sufficient to produce the effect—that is, that some function performed by a gas in rushing into a vacuum was the cause or a circumstance invariably connected with the phenomenon.

The three following hypotheses seemed possible :—

(1) The violent dashing or bombardment of the molecules of air against the glass might have caused the latter to emit light.

(2) It might have been a sort of miniature meteorite phenomenon, caused by the collisions of the fragments of glass with the interior of the receiver and with each other; the

intense bombardment of the larger fragments by the minute dust particles giving rise to the luminous spots.

(3) It might have been an electrical phenomenon caused by the rubbing of air against glass; somewhat resembling that produced by the friction of mercury against glass in a barometric tube*.

In view of testing hypothesis (1) the following experiments were made:—

A bladder was fastened to the neck of a small receiver, the air in which was then exhausted until a vacuum of about 20 millim. was obtained.

The bladder was then caused to burst, and a stream of *yellowish* light was seen to descend within. This experiment was repeated several times with receivers of various heights; and it was found that in the case of tall receivers the light was confined to the higher portion, near the mouth of the receiver.

The intensity of the light seemed to depend upon the pressure in the vacuum, that is to say, upon the violence with which the air entered the interior of the receiver.

The general appearance of this yellowish light seemed to indicate that the luminosity in *this* case was partly, if not altogether, due to parts of the bladder taking fire, being heated by the friction of the air against them, or by being suddenly torn. Articles of various materials, such as those mentioned by Beccaria, were placed in the interior of the receiver, also a plate of glass supported horizontally so that the air on entering might impinge directly upon it.

A light in some respects, perhaps, resembling that mentioned by Beccaria was observed, but only with short receivers; for in the case of tall ones, under precisely similar circumstances, no light was perceived in the lower region where the articles lay; thus suggesting that in the former case the portions of burning bladder had been stopped, in their fall, by the articles within the receiver. Beccaria took no precautions to determine the part played by the bladder in the phenomenon, or rather, he entirely failed to notice that it ever became luminous.

In order to stop the bits of bladder, gauzes of various materials and different thicknesses were tried ; such as should stop the pieces of bladder but permit the air to rush through without much impedance. The glass bottles beneath the gauze, however, were not seen to give rise to any luminosity.

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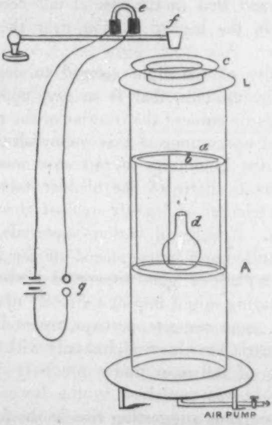
* See Armstrong, Phil. Mag. ser. 3, vol. xviii. (1844).

A similar plan was made use of when air was allowed to enter a vacuum by the breaking of glass.

The apparatus employed for this purpose (see fig. 2) consisted of a cylindrical receiver, A ; a ring, *a*, which fitted closely into the cylinder and was supported by iron rods that were adjustable so that the ring could be moved up and down, carried the wire gauze, *b*, which was tightly fastened to it. A plate of glass, *c*, was laid on the mouth of the receiver, and the contact made air-tight ; *d* were articles such as glass bottles &c. ; an electromagnet, *e*, supported a hammer, *f*, which fell and smashed the glass plate, *c*, when the circuit was broken at *g*. The part of the cylinder above the gauze was screened from the observer's sight.

Fig. 2.



The air in the cylinder having been exhausted, no light was seen to penetrate the gauze, neither was there any luminosity seen in the vicinity of *d*, when the external air was allowed to enter the receiver, in the usual manner, by breaking the glass, *c*.

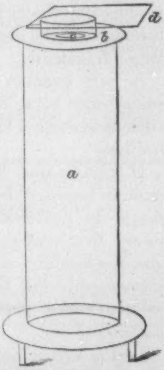
A bladder was then used instead of glass plates, but the results were similar.

Different gases were allowed to issue forth from bottles containing these gases in a highly compressed state, on the surface of glass, and especially on its sharp edges, but without producing any visible effect.

These results do not seem to harmonize with hypothesis (1). Let us now proceed to the consideration of hypothesis (2).

Fig. 3 shows the arrangement by which air could be allowed to enter suddenly into a vacuum without the necessity for breaking glass or bursting a bladder. *a* is the glass receiver; *b* a ring, between which and the receiver is a sheet of fine tissue-paper, *c*, on which a number of fragments of glass were placed; a plate of strong glass situated on top of the ring *b* admitted of being drawn aside, and thus allowed the air to enter the vacuum, whilst the rest of the apparatus was held fast.

Fig. 3.



A luminosity similar to that seen upon previous occasions was observed, though less distinct in some respects, perhaps, than before.

Under precisely similar circumstances, in the absence of any fragments of glass on the tissue-paper, no light was produced, whether or not there were any articles that the air could impinge upon within the receiver.

A single piece of glass cut into a definite shape was then made to take the place of the great number of fragments, some cotton-wool being placed on the plate of the air-pump in order as far as possible to prevent the piece of glass from breaking.

The following facts were noticed :—(*a*) Only a single spark seen. Not as on a previous occasion when a number of fragments of glass were allowed to enter the vacuum,

($\beta$) the spark always appeared on the side of the receiver in the direction in which the plate *d* had been drawn aside * (see fig. 3). ($\gamma$) The piece of glass was found almost vertically under the place where the spark had taken place.

It seemed probable that the spark was caused by the collision of the piece of glass with the interior of the receiver. Two strong pieces of glass were then struck violently together, and a light similar in every respect to that previously observed was produced.

These experiments seem to justify hypothesis (2): the dust particles causing the glow by their impacts against the interior of the receiver and against each other; whilst the brightness of the luminous spots may be attributed to sparks produced by the larger fragments of glass, and to the bombardment of the dust particles against the surfaces of these larger fragments.

A large quantity of fragments of cast-iron, steel, ebonite, sealing-wax, bone, &c., were tried as well as glass, but the attempt to obtain a luminous effect by the above method proved fruitless.

If metallic dust should produce a luminous effect when made to bombard the surface of glass, and if different effects should be produced by lead glass and German glass, the theory that *solid* particles emitted from the kathode would give rise to luminescence of the glass would be justified. The above experiments, however, do not seem to throw much light on Mr. Crookes' theory of luminescence due to the emitted *particles of gas*.

In the earlier stage of the investigation hypothesis (3) appeared plausible enough. Any experiments, however, that were made in connexion with it did not lead to results of an interesting character.

Whatever may be the real value of these experiments, it cannot be doubted that the inquiry into the cause of such a phenomenon as that noticed by Beccaria must prove of the greatest interest: firstly, on account of the obscurity enveloping the subject, and, secondly, on account of the interest attached to the artificial production (though on a small scale) of meteoric phenomena in the laboratory.

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* It is probable *à priori* that this should take place.

# XXVIII. *Students' Simple Apparatus for Determining the Mechanical Equivalent of Heat.* *By* Prof. W. E. AYRTON *and* H. C. HAYCRAFT*.

## I. *The Object to be Attained.*

SOME time ago the authors considered the possibility of constructing an apparatus for the determination of the mechanical equivalent of heat which could be placed in the hands of junior students, and which would enable a sufficiently accurate result to be obtained without the introduction of troublesome corrections. For such a purpose the electrical method was naturally adopted; for now that the commercial values of the electrical units are known with considerable accuracy in the C.G.S. system, it is possible to measure energy in foot-pounds by means of a good commercial ammeter voltmeter and watch with greater ease and certainty than by any mechanical dynamometer.

Further, it has become easy to obtain as much electric power as is wanted for the experiment at a small cost, for the price of half a horse-power for ten minutes is only one-third of a penny, at 6*d*. per Board of Trade Unit. Hence there is not the practical objection to the electrical method that was so formidable when currents of 20 or 30 amperes could only be obtained by setting up a large battery of Grove or Bunsen cells. Indeed every properly organized physical laboratory is now provided with accumulators, from which a quarter or half a horse-power may be readily obtained for use in such experiments as those to be described; or, when accumulators are not available, power may be taken from the mains of one of the numerous electric-supply companies.

## II. *Design of the Apparatus.*

The authors therefore set themselves to design an apparatus which, when used with a good commercial ammeter voltmeter, thermometer, and watch, would give the value of the mechanical equivalent of heat correct to one per cent. without any corrections having to be made even for the heat lost by radiation, convection, and conduction, and without any special manipulative skill being required on the part of the observer.

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* Read November 23, 1894.

Broadly, the experiment consists in passing a known current through a resistance immersed in a known mass of water, and measuring the rise of temperature in a given time, and the average value of the P.D. between the terminals of the resistance.

It is evident that if the loss of heat during the experiment is to be small enough to be neglected in comparison with the quantity of heat generated, either the rise of temperature must be small, or must take place in a very short time, or the ratio of the cooling surface to the mass of the water heated must be small. As it is impracticable to reduce either the rise of temperature or the time to very small limits, and also to measure them with ease and accuracy, it is clear that the result is best obtained by using a large quantity of water, for the ratio of the surface area to the mass can then be made small enough to bring the error due to cooling within the required limits. But a large quantity of water necessarily involves the use of a large amount of electrical energy; and we thus arrive at the result that the accuracy attainable depends upon the amount of *power* at our disposal, and will be greater the greater the electric power that can be supplied.

In designing such an apparatus, then, the first thing to determine is the amount of electric power that can be used, and the details should then be arranged so as to get the least error in the result. In those cases in which an increased accuracy in one measurement involves a diminished accuracy in another, it is best to make the errors due to the two causes equal. For example, suppose that the time during which the electric energy is supplied is such that we can only measure it to one per cent., while the error due to cooling during the experiment is only ½ per cent. We can clearly increase the accuracy of the result if we increase the time until the probable error in reading it is equal to the error due to cooling during that time, say ¾ per cent. If we were still further to increase the time, the error due to cooling would increase and exceed ¾ per cent., and our result would therefore be less accurate. This equality of course does not apply to errors that are not interdependent, such as errors in reading volts and amperes: each of these errors should independently be be made as small as possible.

The measurements to be made are as follows:—

(*a*) The value of the constant current passed through the resistance.

(*b*) The average value of the P.D. between its terminals.

(*c*) The mass of water heated, to which must be added the water-equivalent of the containing vessel, resistance-coil, and stirrer.

(*d*) The rise of temperature of the water.

(*e*) The time during which the current is passed.

With the excellent electrical measuring-instruments now obtainable it is possible to measure either current or pressure with an accuracy much greater than one per cent.; indeed the Board of Trade undertake to measure them within one tenth part of one per cent.* We can also measure the mass of water with considerable accuracy: any error, even a large one, made in determining the water-equivalent of the other bodies raised in temperature becomes of small consequence when the water-equivalent is added to the much larger and accurately measured mass. The measurements (*a*), (*b*), and (*c*), therefore, give us little trouble and do not affect the design of the apparatus.

The case of (*d*) and (*e*) is different. In order to measure a change of temperature by means of a thermometer with the accuracy required, either the change must be fairly large or the thermometer must be very sensitive; but as it is of little use to employ an exceedingly sensitive thermometer to measure the temperature of a liquid which is being locally and rapidly heated, even if the stirring is very efficient, it is necessary to use a fairly large rise of temperature. Similarly, if the circuit is to be closed and broken by hand, and the interval of time measured by an ordinary stop-watch such as would be found in a junior laboratory, there is a certain minimum time required to give the required accuracy of measurement. Also we must keep the ratio of heat lost to heat generated during the experiment equal to the probable error in the time or temperature-measurement; for as these three quantities are interdependent, the best condition is to make the percentage accuracy of the temperature measurement, the percentage accuracy of the time measurement, and the percentage heat lost of heat generated, equal.

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* See Schedule to Final Report of Electrical Standards Committee, 1894.

Let W be the maximum number of watts at our disposal;
M the mass of water, including water-equivalents;
S the area of surface of the containing vessel;
$\epsilon$ the average emissivity of the cooling surface, or the ratio of heat lost in calories per second to the surface area, for 1° C. excess temperature;
$\Theta$ the minimum change of temperature that can be measured to 1 per cent. under the prescribed conditions;
T the minimum time, in seconds, between closing and opening the switch that can be measured by the stop-watch to 1 per cent.;
$\theta$ the rise of temperature of the water;
$t$ the time during which the switch is closed;

and let $\frac{1}{x}$ per cent. be the maximum accuracy of result obtainable under these conditions.

Since $$\theta = x\Theta,$$

and $$t = x\mathrm{T},$$

and the ratio of heat lost to heat received is $\frac{1}{100\,x}$,

we have
$$\frac{\mathrm{S}\,.\,x\frac{\Theta}{2}\,.\,\epsilon\,.\,x\mathrm{T}}{\mathrm{M}\,.\,x\Theta} = \frac{1}{100\,x},$$

or
$$x^2 = \frac{2\mathrm{M}}{100\,\mathrm{S}\,.\,\epsilon\,.\,\mathrm{T}}. \quad . \quad . \quad . \quad (1)$$

We also know, say from preliminary experiments, that the heat received in calories is about 0·24 time the energy in watt-seconds.

$$\mathrm{M}x\Theta = 0{\cdot}24\,\mathrm{W}x\mathrm{T},$$

or

$$\mathrm{M}\Theta = 0{\cdot}24\,\mathrm{WT}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In equations (1) and (2) M and $x$ are the only unknown quantities, for S is a function of M depending on the shape of the vessel containing the water. Thus for a cylindrical vessel of height equal to its diameter,

$$S = 5{\cdot}53\,M^{\frac{2}{3}};$$

while for a spherical vessel,

$$S = 4{\cdot}84\,M^{\frac{2}{3}}.$$

We can therefore find both M and $x$ from the equations, and since

$$\theta = x\Theta,$$

and

$$t = xT,$$

$\theta$ and $t$ are also determined.

It may be observed here that as S varies as $M^{\frac{2}{3}}$, and $x^2$ varies as $\frac{M}{S}$, $x$ is proportional to the 6th root of M or to the 6th root of W. Hence if the number of watts available is doubled the accuracy of the experiments is by no means doubled, but is only increased by about $\frac{1}{8}$th.

In the particular case for which the apparatus was designed the number of watts available was about 300, the maximum current being 30 amperes. This determined the resistance of the coil or strip as $\frac{1}{3}$ of an ohm.

The average emissivity for small excess temperatures of a glass vessel standing on a felt base and containing water was obtained by taking cooling curves, the mean value being 0·000232 calorie per square centimetre of area per 1° C. excess temperature. The water was kept at a uniform temperature by means of a light wooden stirrer during these experiments.

$\Theta$, the minimum rise of temperature that can be measured to one per cent., was taken as 2·5 degrees, as it was not considered advisable to rely on the temperature measurements to more than $\frac{1}{40}$ of a degree. The thermometer used is read without the aid of a telescope, and is graduated in 20ths of a degree.

T, the minimum time that can be read to one per cent., was taken as a minute and a half, as it was thought that an error of nearly a second might be made in the measurement of the time between closing and opening the switch, and stop-watches are often a little doubtful as to their zero.

From equation (2) we have at once

$$M = \frac{0{\cdot}24 \times 300 \times 90}{2{\cdot}5}$$

$$= 2592 \text{ cubic centimetres.}$$

Substituting in equation (1), we have

$$x^2 = \frac{2}{100} \times \frac{\sqrt[3]{2592}}{5{\cdot}53} \times \frac{1}{{\cdot}00023} \times \frac{1}{90},$$

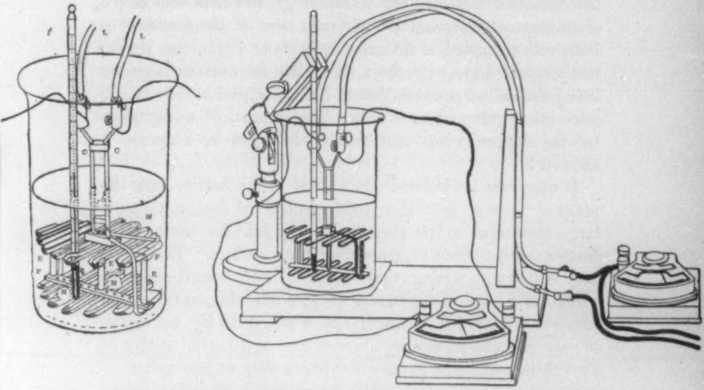
$$x = 1{\cdot}55\,;$$

or the accuracy of measurement is 0·64 of one per cent. The rise of temperature adopted should therefore be 3·87 degrees, the time being 2 minutes 20 seconds. The numbers actually adopted in the experiments were 2000 cubic centim. of water and a time of 2 minutes; the smaller quantity of water being adopted because the resistance of the immersed strip when made proved to be rather less than $\frac{1}{3}$ ohm, the watts taken at 30 amperes being 260 instead of 300.

To ensure success in an experiment of this kind it is necessary that the water be as uniformly heated as possible, and that the stirring be very efficient; and after some consideration the authors decided that the best of all plans would be to use a movable conductor of considerable surface, and so shaped that it might itself be used to stir the liquid. By this means an exceedingly uniform rise of temperature may be produced, every particle of water receiving heat direct from the strip at practically the same rate. The following is a description of the apparatus as constructed by the authors.

A strip of manganin (chosen on account of its low temperature-coefficient), about $\frac{1}{4}$ inch wide, 0·03 inch thick, and about 5 feet long, was bent into a series of zigzags (fig. 1) so as to form a kind of circular gridiron, M M, in which the successive portions of strip lie all in one plane, the whole being held rigid by a strip of vulcanized fibre F crossing the gridiron and to which each portion of strip was screwed. Another precisely similar gridiron was placed 3 inches below the first, and they were held together by three thin ebonite pillars E screwed to the strips of vulcanized fibre, the whole forming the top and bottom of a sort of cylindrical box, 5 inches diameter and 3 inches high. The two grids were joined in series, and the ends of the strip of manganin were soldered to two copper wires C C, about 0·128 inch thick and 6 inches

Fig. 1.



long, which were insulated from one another by vulcanized fibre separators, and constituted a kind of handle by means of which the open box could be moved up and down in the containing vessel.

The whole surface exposed to the water received a thin coat of varnish to prevent any electrolysis due to the difference of potential between the different parts of the strip. At two points in the same vertical line the zigzags forming the two grids are bent so as to leave a space for the passage of a thermometer *t*, the bulb of which is midway between the grids when the lower one is resting on the bottom of the vessel. The whole heating surface exposed to the water is about 60 square inches, or 400 square centimtres. The vessel used to hold the liquid is a thin glass beaker of just sufficient diameter to take the framework of manganin strip.

Electric connexion with the two stiff wires which form the handle is made by means of two well-insulated very flexible leads L L, each composed of a strand of about 210 copper wires ·011 inch diameter. The size of the stout copper wires and of the flexible lead was chosen with the intention that there should neither be heat received nor heat lost on account of these connexions. The sectional area of the insulated flexible lead is rather greater than that of the stout copper wires, and the ultimate rise of temperature of both with a current of 30 amperes is about 7° C.; the rise of temperature during the short time that the current is passed being thus about equal to that of the water, and automatically preventing gain or loss of heat. The number of watts taken by the copper wires and flexible leads at 30 amperes is about 1·9.

It may here be pointed out that it is far better, from the point of view of getting a good mechanical design, to use a large current at a low pressure than to take the same power from a small current at a considerable pressure. Thus it is easy to design a strong stirrer of the shape described above which will have a resistance of $\frac{1}{3}$ of an ohm, carrying 30 amperes at 10 volts pressure; but it would be by no means so easy to make an equally efficient and substantial stirrer of 33·3 ohms resistance to take 3 amperes only at 100 volts.

It was thought worth while to ascertain to what extent conduction through these leads influenced the rate of cooling of the vessel when no current was passing, and cooling curves were therefore taken with the manganin framework in the vessel and attached to the leads. The average rate of cooling was found to be 0·000242 calorie per square centimetre area of surface per 1° C. excess temperature; which is only about 4 per cent. greater than in the previously mentioned experiments, in which a light wooden stirrer only was used, the value then obtained being 0·000232.

## III. *Use of the Apparatus.*

In the following table are given the results of several successive experiments made with the apparatus described above by Messrs. Solomon and Grogan, students at the Central Technical College, under our supervision. The amperes and volts are expressed in the international units adopted at the Chicago Congress. The ammeter and voltmeter used were the well-known Weston-d'Arsonval type instruments. The current was known within about ⅓ of one per cent., and the average potential-difference within about ⅕ of one per cent., the instruments having recently been tested against our standards at the Central Technical College. 2000 cub. centim. of water were used in all the experiments, and were measured with a graduated glass jar, fresh water being used in each experiment. The weight of the glass vessel up to the water-level was determined as 184 grammes, and the specific heat being about 0·2, the water-equivalent is 37 grammes. The weight of the manganin strip is 114 grammes, and the specific heat being about 0·09, the water-equivalent is 10; the equivalent mass of water used being therefore 2047 grammes.

| No. of expt. | Time in seconds. | Temperature. | | | Amperes. | Mean volts. | Calories per watt-second. |
|---|---|---|---|---|---|---|---|
| | | Initial. | Final. | Rise. | | | |
| 1... | 120 | 18·40 | 22·02 | 3·62 | 30 | 8·634 | 0·2383 |
| 2... | 180 | 13·25 | 18·70 | 5·45 | 30 | 8·634 | 0·2390 |
| 3... | 180 | 13·60 | 19·00 | 5·40 | 30 | 8·648 | 0·2367 |
| 4... | 120 | 12·97 | 16·53 | 3·56 | 30 | 8·656 | 0·2375 |
| 5... | 120 | 12·64 | 16·26 | 3·62 | 30 | 8·698 | 0·2365 |
| 6... | 120 | 12·89 | 16·49 | 3·60 | 30 | 8·662 | 0·2364 |
| 7... | 120 | 12·11 | 15·72 | 3·61 | 30 | 8·666 | 0·2368 |
| 8... | 120 | 12·10 | 15·74 | 3·64 | 30 | 8·642 | 0·2395 |
| 9... | 120 | 13·13 | 16·75 | 3·62 | 30 | 8·692 | 0·2367 |

Mean **0·2375**

Average deviation from the mean = ·001 = 0·42 per cent.

With this apparatus, then, we get in about 10 minutes, including the experiment and subsequent calculation, a result for the heat-equivalent of the watt-second; and these results have an average deviation from the mean, if several experiments are made, of less than ½ of one per cent. This result, as we have seen above, should not differ from the true value by as much as one per cent. It may here be pointed out that as the water taken from the ordinary water-supply is sure to be at least two or three degrees below the atmospheric temperature at the time, it is exceedingly easy to arrange that its mean temperature during the experiment shall be exactly equal to the temperature of the air, for no artificial method of cooling is required, as would be the case if a greater range of temperature were used. This, however, was not done except in one or two of the above experiments, and is not necessary to ensure the accuracy that was required.

The mean temperature of the water in the above experiments was 15 degrees Centigrade; and our final result is that at that temperature 0·2375 gramme of water are raised 1° C. in temperature by the energy of one watt-second.

Now we know with considerable accuracy the equivalent in ergs of one watt-second, which certainly does not differ from $10^7$ by more than one tenth of one per cent.; that is to say, the international volt and ampere do not differ from $10^8$ and $10^{-1}$ C.G.S. units of electromotive force and current by more than that amount (see section on the recent history of the electrical units). Hence the result we have obtained, the error in which is less than one per cent., gives us at once a value for the mechanical equivalent of heat with the same accuracy.

Since we find the equivalent of the watt-second in gramme-degrees at 15° C. to be 0·2375, we have at once, taking $10^7$ ergs equal to one watt-second, the mechanical equivalent of heat in ergs per gramme-degree at 15° C. equals **$4{\cdot}211 \times 10^7$**.

Reducing this to foot-lbs. at Greenwich per lb.-degree C. at 15° C., it becomes **1408**, or in foot-lbs. per lb.-degree F. at 59° F. it is **782**.

A series of four experiments made subsequently by some students at the Central Technical College, in which the cooling error was eliminated by making the mean temperature of the water equal to that of the air, gave as their mean 0·2384 calorie per watt-second, or $4{\cdot}195 \times 10^7$ ergs per gramme-degree at about 15° C. Reducing this value to foot-lbs. at Greenwich per lb.-degrees C. and F. respectively, we get 1403 and 779 foot-lbs.

## IV. *Previous Determinations of the Mechanical Equivalent of Heat.*

It is of interest to compare these figures with some of the more recent results obtained for the mechanical equivalent.

Rowland's value for the mechanical equivalent in ergs per gramme-degree at 15° C. is $4{\cdot}189 \times 10^7$, which reduced to foot-lbs. at Greenwich per lb.-degree C. is 1401, and in foot-lbs. per lb.-degree F. at 59° F. is 778·3. Rowland used the method of direct friction of water, and was the first to discover that the specific heat of water was a minimum at 30° C. and varied one per cent. between 5° and 30° C. (Proc. American Acad. 1879–80).

Dieterici (1889) gives as the result of a determination by the electrical method in which Bunsen's ice-calorimeter was used, the number $4·244 \times 10^7$. Correcting from the "legal" ohm employed by him to the international unit, we get the numbers $4·232 \times 10^7$, 1415, and 786 (*Annalen der Physik*, vol. xxxiii. p. 417).

Miculescu's careful determination by the direct method in 1892 gives $4·186 \times 10^7$ on the mercury scale of hard glass, or 4·187 on the hydrogen scale, at about 12° C. The latter number expressed in foot-lbs. at Greenwich per lb. degree C. is 1400, and in foot-lbs. per lb. degree F. is 778. A platinum non-thermal junction was used in these experiments, and was calibrated against a Gonnelot standard mercury thermometer.

Griffiths, using the electrical method, gives as his final result (Proceedings Royal Society, vol. iv. p. 26), $4·198 \times 10^7$, the corresponding numbers in the other units being 1404 and 780.

The recent determination of Schuster and Gannon, also by the electrical method, gives $4·180 \times 10^7$ on the mercury scale of hard French glass, or 4·192 on the hydrogen scale, at a temperature of 19°·1 C. The latter value expressed in foot-lbs. at Greenwich gives 1402 and 779.

Joule's values obtained by friction of water in 1878 gave the numbers $4·159 \times 10^7$, 1390·5, and 772·5 respectively (mercury scale); while his values obtained by the electrical method in 1867, when corrected for the error in the B.A. ohm, give $4·155 \times 10^7$, 1389, and 772, the average temperature of the water being 19° C. The following table gives the results obtained by various methods since 1867, the numbers having been recalculated from those given in a table at the end of M. Miculescu's paper (*Ann. de Chimie*, vol. xxvii. p. 202) :—

| Date. | Observer. | Method. | Ergs per gramme-degree C. | Foot-lbs. per lb.-degree F. |
|---|---|---|---|---|
| 1867. | Joule. | Electrical. | $4{\cdot}155 \times 10^7$ | 772 |
| 1870. | Violle. | Heating of a disk between the poles of a magnet. | $4{\cdot}269 \times 10^7$ | 793 |
| 1875. | Puluj. | Friction of metals. | $4{\cdot}179 \times 10^7$ | 776 |
| 1878. | Joule. | Friction of water. | $4{\cdot}159 \times 10^7$ | 772 |
| 1878. | Weber. | Electrical. | $4{\cdot}145 \times 10^7$ | 770 |
| 1879. | Rowland. | Friction of water 15°. | $4{\cdot}189 \times 10^7$ | 778 |
| 1888. | Perot. | By the relation $L = r(v_2 - v_1)\frac{dp}{dt}$. | $4{\cdot}167 \times 10^7$ | 774 |
| 1889. | Dieterici. | Electrical. | $4{\cdot}232 \times 10^7$ | 786 |
| 1891. | D'Arsonval | Heating of a cylinder in a magnetic field. | $4{\cdot}161 \times 10^7$ | 773 |
| 1892. | Miculescu. | Friction of water. | $4{\cdot}186 \times 10^7$ | 778 |
| 1893. | Griffiths. | Electrical. | $4{\cdot}198 \times 10^7$ | 780 |
| 1894. | Schuster and Gannon. | Electrical. | $4{\cdot}192 \times 10^7$ | 779 |

The results obtained since 1879 by stirring water and by electrical methods may be tabulated thus :—

| | |
|---|---|
| Rowland (friction) | $4{\cdot}189 \times 10^7$ or 778, |
| Dieterici (electrical) | $4{\cdot}232 \times 10^7$ or 786, |
| Miculescu (friction) | $4{\cdot}186 \times 10^7$ or 778, |
| Griffiths (electrical) | $4{\cdot}198 \times 10^7$ or 780, |
| Schuster and Gannon. (electrical) | $4{\cdot}192 \times 10^7$ or 779. |

The result obtained by our students is greater than the mean of these results by just one half per cent. It is probably not generally known that such accuracy can be obtained by the use of such simple apparatus as that here described, and the fact is we think sufficient justification for bringing the result under the notice of the Society.

### V. *Recent History of the Practical Electrical Units.*

A short account of the recent history of the practical electrical units is added for the benefit of those not familiar with the work of the Board of Trade Standards Committee.

The first report of the Electrical Standards Committee, appointed by the Board of Trade at the end of 1890, was presented in July 1891, and contained the following recommendations among others :—

"4. That the resistance offered to an unvarying electric current by a column of mercury of a constant cross sectional area of one square millimetre and of a length of 106·3 centimetres, at the temperature of melting ice, may be adopted as one ohm."

"10. That an unvarying current, which when passed through a solution of nitrate of silver in water, in accordance with the specification attached to this Report, deposits silver at the rate of 0·001118 of a gramme per second, may be taken as a current of one ampere."

At the British Association meeting held at Edinburgh in August 1892 the B.A. Committee on Electrical Standards, in consultation with Dr. von Helmholtz, M. Guilleaume, Professor Carhart, and others, agreed to the following resolutions among others :—

"2. That 14·4521 grammes of mercury in the form of a column of uniform cross section 106·3 centimetres in length at 0° C. be the specified column of mercury adopted as the practical unit of resistance."

"That the number ·001118 should be adopted as the number of grammes of silver deposited per second from a neutral solution of nitrate of silver by a current of 1 ampere, and the value 1·434 as the electromotive force in volts of a Clark cell at 15° C."

These decisions agreed with those which had already been laid before the German Government by Dr. Helmholtz and the Curatorium of the Reichsanstalt. It was considered preferable to define the mercury column in terms of length and mass, as the sectional area cannot be directly measured with such accuracy; but the length 106·3 centimetres was adopted so that the sectional area might be, as nearly as could be known, one square millimetre, as this area has been specified in all previous definitions.

In November 1892 a supplementary report was presented to the Board of Trade by its Standards Committee, and included the following resolutions :—

"4. That the resistance offered to an unvarying electric current by a column of mercury at the temperature of melting ice 14·4521 grammes in mass of a constant cross sectional area, and of a length of 106·3 centimetres, may be adopted as one ohm."

"10. That an unvarying current which, when passed through a solution of nitrate of silver in water, in accordance with the specification attached to this Report, deposits silver at the rate of 0·001118 of a gramme per second, may be taken as a current of one ampere."

"14. That the electrical pressure at a temperature of 15° Centigrade between the poles or electrodes of the voltaic cell known as Clark's cell, prepared in accordance with the specification attached to this Report, may be taken as not differing from a pressure of 1·434 volts by more than one part in one thousand."

At the International Electrical Congress held in August 1893 at Chicago these values were adopted by the delegates as those to be recommended to their several governments as legal units.

The Board of Trade Committee, after having had laid before them the recommendation of the Electrical Congress, which was substantially that contained in their supplementary report of November 1892, presented their final report advising a legalization of the standards as defined, by an Order of Her Majesty in Council; and on August 23rd, 1894, this was effected, and the practical standards we may hope permanently settled.

Of the three units—ohm, ampere, and volt—the two former are defined on the C.G.S. system, and the latter as a secondary unit from the relation of the first two. The numbers given in the above-quoted resolutions as to the ohm and the ampere are the values which appear to represent most accurately the true volt and the true ampere. In the Report of the B.A. Standards Committee for 1892 is given a table showing the results of nine determinations of the ohm expressed in centimetres of mercury, made between 1882 and 1892; the mean of these results being 106·31, and the average deviation from this mean being ·015, or one part in 7000. We may therefore safely say that the ohm, as now defined, does not differ from $10^9$ C.G.S. units of resistance by more than one part in two or three thousand.

As regards the ampere, we have the very careful determination of Lord Rayleigh and Mrs. Sidgwick giving ·0011179 gramme of silver per coulomb, that of Kohlrausch ·0011183, Gray ·001118, and Potier and Pellat ·0011192. It is at least probable that the value ·001118 adopted by the Board of Trade Committee does not differ from that corresponding to the absolute C.G.S. unit divided by ten by more than one part in a thousand.

Hence it is probable that the number of ergs equivalent to one watt-second does not differ from $10^7$ by more than one part in a thousand; and that being the case it would seem that, considering the great accuracy with which electrical measurements can be made, the electrical method of determining the mechanical equivalent of heat should be the most accurate.

## DISCUSSION.

Mr. GRIFFITHS thought it unadvisable to provide junior students with apparatus from which every source of error had been eliminated; they were thus led to underrate the difficulty of an experiment and the care required to obtain reasonable accuracy.

Prof. CAREY FOSTER agreed generally with Mr. Griffiths, and deprecated the use of direct-reading am-meters and volt-meters in experiments of this kind. He thought it preferable that a student should learn to reduce instrumental readings to absolute measure for himself.

Prof. S. P. THOMPSON dissented from the opinions expressed by the two previous speakers, and thought it was an advantage to students to have the use of direct-reading instruments.

Dr. SUMPNER described a simple method which he had employed for measuring the mechanical equivalent of heat, and which depended on the heating of a stream of water as it flowed through a pipe containing the current conductor.

Prof. RÜCKER was inclined to take an intermediate view of the questions that had been raised. He thought that students should take for granted as little as possible concerning their instruments, but to verify every point, even if practicable, would occupy much time that might be otherwise more profitably employed.

Prof. AYRTON replied, and explained that the calibration of am-meters and volt-meters would be part of the work of a student at another part of his course.

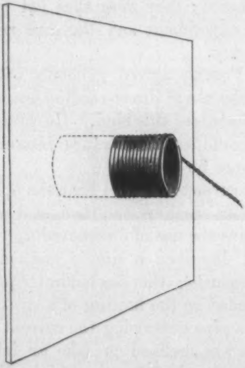
# XXIX. *Mirrors of Magnetism.*

*By* SILVANUS P. THOMPSON, *F.R.S., and* MILES WALKER[*].

OUR knowledge of Electric Images is based almost entirely upon mathematical deduction. It would be difficult to satisfactorily demonstrate their properties by experiment. We are content to take the elegant geometrical proofs that Lord Kelvin has given us, and corroborate these physically at points where the conclusions are within reach of experiment. The subject, therefore, is one of purely theoretical interest, but so beautifully does it elucidate difficult problems in Electrostatics that it remains the continual delight of text-book writers.

Magnetic Images, on the other hand (apart from one or two investigations by the same great master), are entirely neglected, and yet these are much more likely to be practically utilized in the near future than their electrical analogues. It may be in questions of dynamo and instrument shielding, or it may even be in the solution of that commercial problem, the testing of the magnetic properties of iron *en masse.*

Fig. 1.



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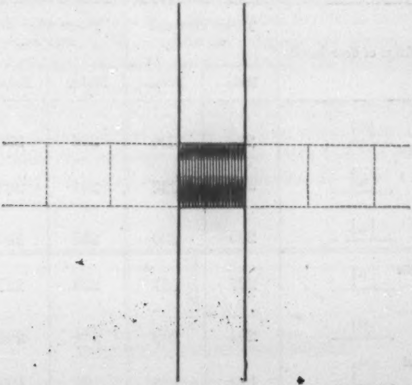
[*] Read November 23, 1894.

The existence of magnetic images is suggested by considerations altogether apart from the mathematical.

If we take a solenoid of wire through which a current is flowing and place its end against a large plate of iron, we eliminate the effect of that end upon the distribution of the field about the coil, and so obtain a field on one side of the plate of a shape the same as if the coil were continued to double its length. If we place the coil with its end against a mirror (fig. 1), we see it reflected in the mirror so that it appears to be double its real length. Thus the iron plate gives us magnetically an image of the coil analogous to the optical image produced by the mirror, geometrically identical indeed with the optical image, virtual and erect.

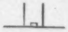
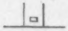
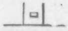
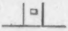
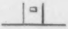
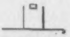
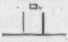
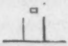
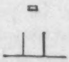
Fig. 2.



If a large iron plate is placed at each end of the coil the field will be the same as if the coil were infinitely long. We know that two mirrors, facing each other, one at each end of the coil, would give it the appearance of stretching away to infinity in both directions (fig. 2).

Of course these optical effects could only be perfectly obtained if the mirror were a perfect reflector; and to include all possible points of view it would have to be infinitely large. So the magnetic effects could only be perfectly obtained if the plates were perfectly permeable and infinitely large. Observe that we are only considering the effect at a point *in front* of the mirror and in front of the iron plate. *Behind*, that is to say on the side opposite the coil, there is no effect in either case.

It was thought interesting to ascertain how far effects of this kind could be obtained in practice, using an ordinary iron plate somewhat less than that required for the perfect case. For this purpose two similar solenoids were wound, 5 centim. long and 4 centim. mean diameter, the winding at the ends being exposed so that it could be put up close to the iron. A search-coil of 100 turns, about 1½ centim. in diameter, was mounted so that it could be fixed at different positions relatively to one of the solenoids, which was then

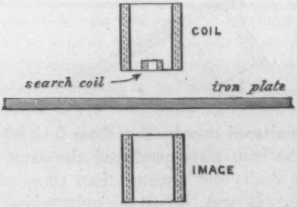
| Position of Search-coil. | Throw when coil on coil. | | Throw when coil on iron. | |
|---|---|---|---|---|
| | Make. | Break. | Make. | Break. |
|  | 236 | 236 | 236 | 235 |
|  | 235 | 235 | 234 | 234 |
|  | 230 | 230 | 230 | 229 |
| middle  | 227 | 227 | 228 | 227 |
|  | 204 | 202 | 204 | 202 |
| end  | 129 | 126 | 129 | 127 |
|  | 69 | 67 | 69 | 68 |
|  | 41 | 41 | 41 | 41 |
|  | 24 | 24 | 24 | 23 |

placed upon the iron plate* and upon the other solenoid alternately. A current of constant value was turned on and off in each position of the solenoid, and the throw on a ballistic galvanometer in the circuit of the search-coil observed. The preceding table, giving the throw of the needle for different positions of the search-coil, shows how perfectly the iron plate mirrored the magnetism of the solenoid. The discrepancy in the figures arises more from errors of observation than anything else.

The first position in the above table is the most important, as the coil is placed in a part of the field that experiences the greatest change by the presence or absence of the iron plate, the difference being that between 236 and 129. If the search-coil could have been placed so that its centre was at the very end of the solenoid, the throw ought to be just one half of what it would be with the coil continued to double its length. This was found to be so when the solenoid was placed on the other solenoid, but could not be tried with the iron as part of the search-coil protruded.

The experiment was then made of lifting the solenoid step by step a little distance from the iron plate, when it was found that the presence of the iron plate had the effect of producing an image of the coil receding an equal amount behind the plate.

Fig. 3.



A larger search-coil was placed in different positions outside the solenoid; and in all positions on which any readable throw of the needle could be obtained, it was found that the iron plate gave an effect almost exactly the same as an equal solenoid in the position of its image.

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* The iron plate was ordinary boiler-plate ½ inch thick, size 3 feet by 2 feet.

In order to try the effect of tilting the solenoid, it was mounted on a strip of wood hinged to another, the angle between them being fixed by a clamp (fig. 4.) This was then placed alternately on the iron plate and against a similar hinged strip upon which the other solenoid was placed, the angle of inclination being the same for both solenoids (fig. 5).

Fig. 4.

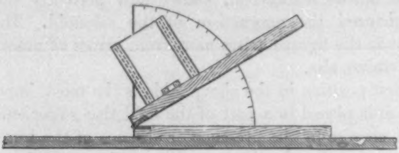
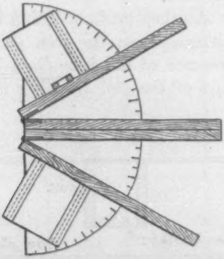


Fig. 5.



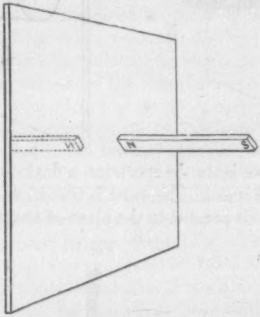
The angle was altered step by step from 0 to 90 degrees, and in all cases the iron plate produced the same effect as its image within limits not greater than those shown in the previous table. It was, however, only when the solenoid was placed at the end of the hinged strip nearest the iron plate that readings of any value could be obtained, as small dislocations in the position of the coil laterally were apt to produce changes of reading comparable with those due to considerable changes in angle. At distances greater than

5 centim. the iron had very little effect. The search-coil during these experiments was moved about to different positions both inside and outside the solenoid, preference being given to the most sensitive positions.

Then the effect of differently-shaped solenoids was tried. A long narrow one and a wide flat one were used with similar effects, so far as they could be measured.

There is a difference between the magnetic reflexion of an iron plate and the optical reflexion of a mirror in the following respect: an optical image has those of its lines which are at right angles to the mirror reversed while those parallel to the mirror are not reversed. For instance, if we hold a magnet with its north end pointing from us and towards a mirror, the optical image of it will have its North end pointing towards us (fig. 6). But in the case of a magnetic image this is inversed: the magnetic image has its South end pointing towards us. In fact the reflexion of a North end is a South end. If, however, we look at the reflexion of the currents flowing in the solenoid instead of at the sign of the pole of the solenoid, we see that laws of the optical case hold good for the magnetic case. The image (fig. 7) of a current flowing in any direction in a plane parallel to the mirror is another current flowing parallel to the first and towards the same part.

Fig. 6.



A North pole viewed from the front is equivalent to a lævocheiral circulation of current. The image of this pole turned towards the mirror is, to the spectator, a dextro-cheiral circulation, or a South pole. The same is true if, as in fig. 8, the solenoid has its axis parallel to the plane of the mirror.

Fig. 7.

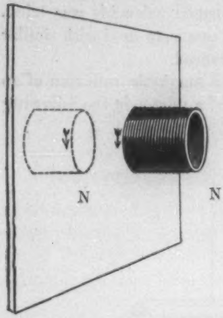


Fig. 8.

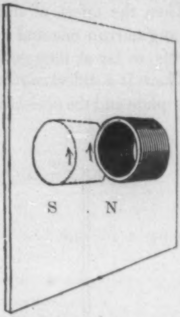
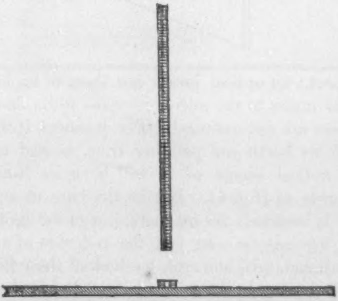


Fig. 9.

Fig. 10.

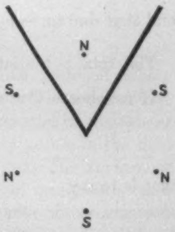


In order to try some effects with an isolated pole, a solenoid, 2 metres long and 1·5 centim. mean diameter, was uniformly wound with twelve turns per centimetre of a suitable wire. When a current of 15 amperes was passed through this a pole of a strength of about 40 units (C.G.S.) was obtained, and this might be regarded as an isolated pole at distances not greater than 30 centim. from it. It was found that bringing an iron plate within a few centimetres of this pole produced very nearly the same effect upon the field as would have been produced by bringing up a pole of opposite sign to a point at double the distance.

The field close to the iron plate ought to have been exactly twice as strong as if no iron plate were there. This was found to be so within the limits of error of observation (about 3 per cent.) when the pole was within 6 centim. of the iron plate. As the distance was increased the throw of the needle became too small to be accurately read, and the field being extremely weak the susceptibility of the iron would be very low.

It was this weakness of the field (for one could not consider the pole as a point except at distances exceeding 10 centim.) that spoilt some experiments on kaleidoscope effects. One can conceive that if the laws of reflexion hold good between a magnetic pole and a sheet of iron, it ought to be possible, by means of several sheets of iron, to build up a magnetic kaleidoscope by which the effect of a great number of magnetic poles could be produced from a single pole. The idea of a magnetic kaleidoscope was suggested by Lord Kelvin many years ago, but it is doubtful whether it has ever been successfully carried out. If, for instance, two plates of susceptible material are inclined to each other at an angle of 60 degrees, and the North pole of a magnet placed evenly between them, one would expect to get between the plates exactly the same distribution of field as if there were six poles, three norths and three souths, spaced alternately and evenly round the line of intersection of the plates. It may, however, be said to those who would care to try this experiment, that they must use a point pole of much greater strength than 40 units, or plates much more susceptible than iron if they hope to be at all successful.

Fig. 11.

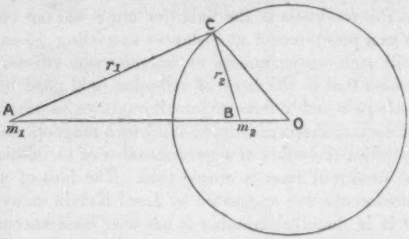


The close connexion between the effect of an iron plate magnetically and that of a mirror optically naturally makes us ask what would be the effect of a curved plate? Would it give magnified or diminished images like a concave or convex mirror, and what would be the position of these images with regard to the object?

If we take the case of spherical curvature, and consider the iron as being infinitely susceptible, the answer to these questions can be determined theoretically from the laws of magnetic potential. All the formulæ relating to electric images already known are applicable to magnetic images.

If we consider two points A and B at which are placed two poles respectively, of the strengths $+m_1$ and $-m_2$, the magnetic potential at a point C due to $m_1$ is $\frac{m_1}{r_1}$ where $r_1 = AC$, and that due to $-m_2$ is $-\frac{m_2}{r_2}$ where $r_2 = BC$.

Fig. 12.



The total potential at C is therefore $\frac{m_1}{r_1} - \frac{m_2}{r_2}$.

If we choose C at a point of zero potential, we have

$$\frac{m_1}{r_1} - \frac{m_2}{r_2} = 0;$$

that is to say

$$\frac{m_1}{m_2} = \frac{r_1}{r_2};$$

but $\frac{m_1}{m_2}$ is a constant; therefore, if we take C at the points of zero potential $\frac{r_1}{r_2}$ will always be constant. But if a point moves so that $\frac{r_1}{r_2}$ remains constant it moves on the surface of a sphere, therefore the equipotential surface of value zero is in the form of a spherical shell. If O be the centre of the sphere, it follows from a well-known property of a circle that

$$\frac{\mathrm{AO}}{\mathrm{OC}} = \frac{r_1}{r_2} = \frac{m_1}{m_2}.$$

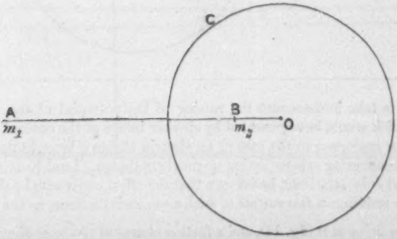
If, therefore, we are given $m_1$ we can find from the equation

$$m_2 = m_1 \frac{\mathrm{OC}}{\mathrm{AO}},$$

the strength of pole $m_2$ which when placed at B will give zero potential on a given spherical shell.

Now consider a magnet pole $+m_1$ (fig. 13) brought up to

Fig. 13.



a point A near a sphere of very susceptible material whose radius is large as compared with the distance between A and its surface, so that we may neglect the potential of the sphere due to $m_1$ in dealing with the potential of points in the field we are considering, and so that we may take the surface of the sphere as an equipotential surface of practically zero value *. The distribution of the field outside the sphere will

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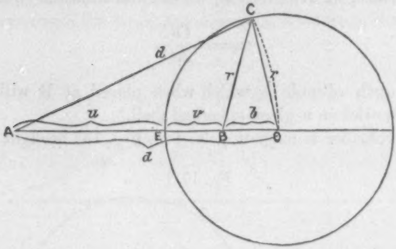
* [*Note added after reading of Paper.*—At this point our original paper contained the following remark as a footnote :—" If the magnetic object is large, or is far removed, then besides the image as above defined it is

be the same as if no sphere were there, but instead a pole of strength $-m_1\frac{\mathrm{OC}}{\mathrm{AO}}$ were placed at B. We may say that the sphere acting like a convex mirror has given a diminished image at B.

We can find the position of B by the following construction:—Describe the arc OC (fig. 14) with A as a centre, and then describe the arc OB with C as a centre, B being on the

Fig. 14.



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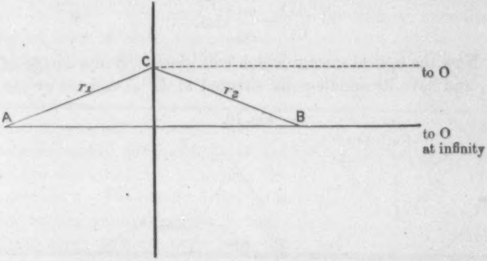
necessary to take into account the raising of the potential of the whole sphere, which would be represented by another image at the centre." The case is then analogous to the case of an electric charge $q$ brought up to an insulated conducting sphere having no previous charge. Lord Kelvin, in a paper dated July 7th, 1848, has shown that the effect on external points of the charge residing on the surface of such a sphere is the same as the effect of a charge $-\frac{r}{d}q$ at B (fig. 14), and a further charge of $+\frac{r}{d}q$ at the centre O. His reasoning being applicable to the magnetic case, we see that the image of a North pole at A consists of a doublet having a South pole situated at B of strength $m_1\frac{r}{d}$ and a North pole also of the strength $m_1\frac{r}{d}$ situated at the centre O. Now any magnetic object such as a solenoid will have a South pole as well as a North pole, and if the object is small compared with the size of the sphere, both North and South may be taken as equidistant from the centre, and their images at the centre will therefore neutralize each other, and we have left the image that is considered in the text. If the object is large as compared with the size of the sphere, then in both the magnetic case and the optical case there is a confusion of images.]

line AO. The condition that $\frac{r_1}{r_2}$ shall be constant for all points on the circumference is that $\frac{\mathrm{OC}}{\mathrm{BO}}$ shall be equal to $\frac{\mathrm{AO}}{\mathrm{OC}}$, and this is seen to be true from the similarity of the triangles ACO and COB.

If we had any number of magnetic points outside the sphere each would have its virtual image inside the sphere; thus any form of magnet, such as a solenoid carrying a current, would also have its image.

It is easy to see that the experiments above mentioned with a large iron plate can be explained in this way. For if we may consider the plate as part of an infinite sphere:

Fig. 15.



in this case $\frac{\mathrm{AO}}{\mathrm{OC}}=1$; therefore $\frac{m_1}{m_2}=1$; therefore $m_1=m_2$: and further $\frac{r_1}{r_2}=1$; therefore $r_1=r_2$.

To assimilate to optical formulæ let us now express the relations in terms of the distance of object and image respectively from the pole E of the mirror, and write $\mathrm{AO}=d$; $\mathrm{BO}=b$; $u=\mathrm{AE}=d-r$; $v=\mathrm{BE}=r-b$ (fig. 14). Now

$$\frac{d}{r}=\frac{r}{b}, \text{ by similar triangles.}$$

This may be written

$$\frac{u+r}{r}=\frac{r}{r-v};$$

whence

$$\frac{1}{u}+\frac{1}{r}=\frac{1}{v}.$$

The well-known optical mirror formula for a spherical mirror differs from this in having $\frac{2}{r}$ instead of $\frac{1}{r}$.

In order that a magnetic image as at B in fig. 14 should be produced by a magnetic object at A, and with the relative strengths $m_2$ and $m_1$, not only must the reflecting surface pass through the point E such that

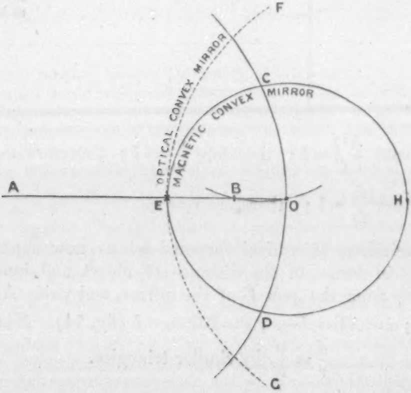
$$\frac{\mathrm{AE}}{\mathrm{BE}}=\frac{m_1}{m_2},$$

but the curvature of the magnetic mirror is defined by the condition previously laid down that

$$\frac{\mathrm{AO}}{\mathrm{CO}}=\frac{m_1}{m_2} \text{ also.}$$

Now the optical mirror which will give at B the image of A, and have its middle-point situated at E (as defined by the former of these conditions) will not have O for its centre. In fact it will be a spherical surface having half the curvature or twice the radius. If (fig. 16) the dotted circle FEG be

Fig. 16.



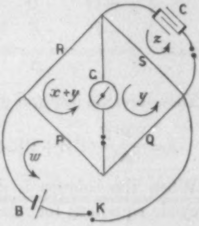
drawn with centre H, we have the sectional view of the optical convex mirror which will give the same position of image as the magnetic convex mirror shown by the circle CED.

In conclusion, it may be remarked that the construction of fig. 14 affords a new and simple graphic method of finding the position of optical images, by the device of using the auxiliary circle whose diameter is the radius of the spherical surface.

## XXX. *A Modification of the Ballistic-Galvanometer Method of Determining the Electromagnetic Capacity of a Condenser.*

*By* F. WOMACK*.

THE method consists in placing the condenser in parallel with one arm S of a Wheatstone-bridge arrangement of non-inductive resistances. A balance for steady currents having been obtained, the condenser is placed in circuit, and the throw $\theta$ determined due to the depression of the battery-key. The condenser is then thrown out of circuit, and the proportionality of the arms of the bridge disturbed by changing the value of S. The steady deflexion $\alpha$ due to this want of balance is read. From these two readings and the known values of S, the capacity is immediately determined.



If $x$, $y$, $z$, $w$ denote the integral cyclic currents reckoned from the instant of make,

$$\left.\begin{aligned} P(x+y-w)+\quad Gx\quad &+R(x+y)=0\\ -Gx\quad +Q(y-w)&+S(y-z)=0\\ P(w-x-y)+\quad Bw\quad &+Q(w-y)=\int E\,.\,dt\\ &z=CS\dot{y}_\infty \end{aligned}\right\}$$

Substituting for $z$ in the second equation and rearranging,

$$\left.\begin{aligned} (P+G+R)x+(P+R)y-\qquad Pw\quad &=0\\ -Gx\quad +(Q+S)y-\qquad Qw\quad &=CS^2\dot{y}_\infty\\ -Px\quad -(P+Q)y+(P+Q+B)w&=\int E\,.\,dt \end{aligned}\right\}\begin{matrix}\text{(i.)}\\ \text{(ii.)}\\ \text{(iii.)}\end{matrix}$$

---

* Read November 23, 1894.

Hence

$$x=\frac{\begin{vmatrix} 0 & P+R & -P \\ CS^2\dot{y}_\infty & Q+S & -Q \\ \int E\,.\,dt & -(P+Q) & P+Q+B \end{vmatrix}}{\begin{vmatrix} P+G+R & P+R & -P \\ -G & Q+S & -Q \\ -P & -(P+Q) & P+Q+B \end{vmatrix}}=\frac{CS^2\dot{y}_\infty \begin{vmatrix} -(P+Q) & P+Q+B \\ P+R & -P \end{vmatrix}}{\Delta}$$

$$=\frac{CS^2\dot{y}_\infty}{\Delta}(PB+PR+QR+BR).$$

To find the steady current $\dot{y}_\infty$ ultimately flowing through S we have the same equations, except that the right-hand side of (ii.) is zero, and $\dot{x}_\infty$, $\dot{y}_\infty$, $\dot{w}_\infty$ instead of $x$, $y$, $w$. Hence

$$\dot{y}_\infty=\frac{\begin{vmatrix} P+G+R & 0 & -P \\ -G & 0 & -Q \\ -P & E & P+Q+B \end{vmatrix}}{\Delta}=\frac{E}{\Delta}(PQ+GQ+RQ+PG).$$

Therefore the integral current through the galvanometer is

$$x=\frac{CS^2E}{\Delta^2}(PB+PR+QR+BR)(PQ+GQ+RQ+PG).$$

When the balance is disturbed by S becoming S$+d$S, the cyclic equations for steady currents are

$$\left.\begin{array}{lllll} (P+G+R)\dot{x}_\infty + & (P+R)\dot{y}_\infty & - & P\dot{w}_\infty & =0 \\ -G\dot{x}_\infty & +(Q+S+dS)\dot{y}_\infty - & & Q\dot{w}_\infty & =0 \\ -P\dot{x}_\infty & - \quad (P+Q)\dot{y}_\infty & & +(P+Q+B)\dot{w}_\infty & =E \end{array}\right\},$$

which give

$$\dot{x}_\infty=\frac{\begin{vmatrix} 0 & P+R & -P \\ 0 & Q+S+dS & -Q \\ E & -(P+Q) & P+Q+B \end{vmatrix}}{\Delta \text{ nearly}}=\frac{EP}{\Delta \text{ nearly}}dS,$$

assuming the value of the determinant $\Delta$ to be but little affected by the change of S.

Therefore, finally,

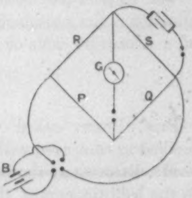
$$\frac{x}{\dot{x}_0}=\frac{\mathrm{T}}{2\pi}\cdot\frac{2\sin\theta/2}{\tan\alpha}\times\text{ correction for damping}$$

$$=\frac{\mathrm{CS}^2}{\Delta}\cdot\frac{(\mathrm{PB}+\mathrm{PR}+\mathrm{QR}+\mathrm{BR})(\mathrm{PQ}+\mathrm{GQ}+\mathrm{RQ}+\mathrm{PG})}{\mathrm{P}\,.\,d\mathrm{S}},$$

which on expansion of $\Delta$ gives $\frac{\mathrm{CS}^2}{d\mathrm{S}}$;

$$\therefore\quad \mathrm{C}=\frac{\mathrm{T}}{2\pi}\cdot\frac{2\sin\theta/2}{\tan\alpha}\cdot\frac{d\mathrm{S}}{\mathrm{S}^2}\times\text{ correction for damping.}$$

In the practice of the method, in order to avoid error arising from the altered value of $\Delta$ due to the change of S, readings of the deflexion, $\alpha$ may be taken with equal positive and negative values of $d$S. Thus an error which otherwise might be as great as 1 in 100 is reduced to 1 in $10^4$.



In order to avoid change of the E.M.F of the battery due to its being for any appreciable time on open circuit, it is desirable to use a reversing-key in the battery branch, and to observe the throw of the galvanometer due to reversal of the sign of the current in S ; and immediately after observe the deflexion due to the alteration of S.

The method is necessarily subject to the same disadvantages as that of Fleeming Jenkin, in respect of it not giving the instantaneous capacity of the condenser. But measurements of the same condenser taken with different galvanometers, or with a graded moment of inertia of the galvanometer-needle, have led to nearly constant results, the capacity being apparently but little dependent on the period of charging and discharging of the condenser. The effect would be likely to be much more marked if the capacity were much greater.

The conditions for a maximum throw of the galvanometer for a given E.M.F. are, moreover, not the same as those for the maximum sensitiveness to steady current. There is usually no difficulty, however, in obtaining sufficient sensitiveness of galvanometer to detect want of proportionality of the arms P Q R S of the bridge, so that a change of S by 1 in 200 will thus give a deflexion of convenient magnitude. It is, however, very advantageous to have a galvanometer whose period of oscillation can be varied at pleasure, so as to give about the same throw as steady deflexion for the chosen value of $dS$. One advantage which the method has is that there is no necessity to know the galvanometer or battery resistance. In the ordinary ballistic-galvanometer method it is very doubtful if the resistance of the galvanometer, unless it is measured at the time, is known within 1 to 2 per cent.

Further, the two essential parts of the determination $\theta$ and $a$ may be made in quick succession, without any shifting of contacts or connexions and with the battery-current flowing continuously, leaving only the period of the galvanometer and its damping correction to be afterwards determined.

The method may be of service in the simultaneous determination of the resistance of, and joint capacity and inductance of, a submarine cable or telephone- or telegraph-line.

## Discussion.

Prof. **Perry** asked what were the advantages of the method as compared with the Rayleigh-Sumpner method.

Mr. **Blakesley** thought that the correction for damping in the ballistic part of the experiment might be avoided, if, in the second part, the disturbance of balance due to the increment of S were measured by half the first throw of the needle on making the galvanometer circuit, instead of by the steady deflexion. He doubted whether reversing the current in the battery circuit would have just twice the effect of simply breaking the circuit.

In reply, Mr. **Womack** said he had not tried the method of reading suggested by Mr. Blakesley; but with regard to the reversing of the battery circuit, that was found to give in practice as nearly as possible twice the deflexion which resulted from simply breaking.

## XXXI. *On the Determination of Thermal Conductivity and Emissivity.* *By* N. EUMORFOPOULOS, *B.Sc., Demonstrator in Physics, University College, London*[*].

IF a long metallic bar of uniform cross-section be heated at one end, and be left long enough to acquire a steady state, the distribution of temperature along it is usually expressed by

$$u_x = u_0 e^{-x\sqrt{\frac{hp}{ks}}},$$

where $u_x$ is the excess of temperature over surroundings of a point on the bar at a distance $x$ from the point whose excess of temperature is $u_0$, $x$ being measured positively along the direction of decreasing temperatures;

$h$ and $k$ are the emissivity and conductivity respectively;

$p$ is the periphery of the bar, and $s$ the cross-section.

If the bar be of circular cross-section and $r$ its radius, the above expression reduces to

$$u_x = u_0 e^{-x\sqrt{\frac{2h}{kr}}};$$

that is, if two bars have at one point of each the same temperature $u_0$, they will also have the same temperature $u_x$ at distances $x_1$ and $x_2$ respectively, measured from these points, and such that

$$x_1\sqrt{\frac{h_1}{k_1 r_1}} = x_2\sqrt{\frac{h_2}{k_2 r_2}}.$$

If the bars are of different radii, but of the same material, and we accordingly write $h_1 = h_2$ and $k_1 = k_2$, we get

$$\frac{x_1}{x_2} = \sqrt{\frac{r_1}{r_2}}.$$

Some time ago Prof. G. C. Foster suggested to me, as a laboratory exercise, to undertake the verification of this relation.

The method adopted was to heat the ends of two such rods in steam until they had acquired the steady state, and then by means of two thermoelectric joints (one on each rod) to find a series of isothermal points.

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[*] Read January 11, 1895.

With two *brass* rods of radii $r_1=3{\cdot}4$ and $r_2=2{\cdot}6$ mm. respectively, the distances at which equal temperatures were found were as follows :—

$$\sqrt{\frac{r_2}{r_1}}=0{\cdot}87.$$

| $x_1$. | $x_2$ | $\frac{x_2}{x_1}$ |
|---|---|---|
| 20 mm. | 13 mm. | ·65 |
| 40 | 29 | ·72 |
| 60 | 42 | ·70 |
| 85 | 64 | ·75 |
| 110 | 78 | ·71 |

Mean = ·71

Similar experiments with *copper* rods gave :—

$$r_1=3{\cdot}35 \text{ mm.}, \quad r_2=2{\cdot}45 \text{ mm.} \quad \sqrt{\frac{r_2}{r_1}}=0{\cdot}86.$$

| $x_1$. | $x_2$. | $\frac{x_2}{x_1}$. |
|---|---|---|
| 20 mm. | 18 mm. | ·90 |
| 40 | 25 | ·62 |
| 60 | 34 | ·57 |
| 80 | 47 | ·59 |
| 100 | 61 | ·61 |

In the first value of $\frac{x_2}{x_1}$ some error has, no doubt, crept in.

Mean of last four = ·60.

Another set of experiments with the same rods gave :—

| $x_1$. | $x_2$. | $\frac{x_2}{x}$. |
|---|---|---|
| 20 mm. | 10 mm. | ·50 |
| 40 | 22 | ·55 |
| 20 | 11 | ·55 |
| 40 | 22 | ·55 |
| 20 | 12 | ·60 |

Mean = ·55

To ascertain whether the copper rods really consisted of the same metal, their specific electrical resistances were compared. The result was

$$\frac{\rho_1}{\rho_2} = \cdot 80.$$

Assuming that the ratio of thermal conductivities was the same as that of electrical conductivities, this gives

$$\frac{x_2}{x_1} = \sqrt{\frac{k_2 r_2}{k_1 r_1}} = \cdot 77$$

as the calculated ratio of the distances at which equal temperatures should be found, instead of ·60 and ·55, the mean ratios actually found in the two sets of experiments already mentioned.

In order to test the trustworthiness of the method employed, one of the above rods was heated in the middle under the same conditions as before, and isothermal points found on each side of the heated portion. The results were satisfactory, as the following numbers show :—

| $x$. | $x_1$. |
|---|---|
| 20 mm. | 19 mm. |
| 40 | 40 |
| 60 | 61 |
| 80 | 81 |

At this point the experiments were abandoned for a time. They were subsequently resumed, when a Bunsen burner was used as the source of heat, in order to have a greater range of temperature. In the experiments mentioned before, and also in these, no screens were employed, a sheltered part of the laboratory being used. The following are some of the results obtained :—

*German Silver Rods.*

$$r_1 = 3{\cdot}0 \text{ mm.}, \quad r_2 = 2{\cdot}5 \text{ mm.}, \quad \sqrt{\frac{r_2}{r_1}} = \cdot 91.$$

Making $x_2 = 10{\cdot}3$ cm., $x_1 = 11{\cdot}95$ cm. as a mean of five determinations, or

$$\frac{x_2}{x_1} = \cdot 86.$$

As a mean of a large number of experiments, making $x_2=10{\cdot}0$ cm., $x_1$ was found to be 11·68 cm., or

$$\frac{x_2}{x_1}=\cdot 86.$$

The arrangements were then slightly changed, so as to experiment on a hotter part of the rod, with the following result as a mean of a series of experiments :—

$x_2=10{\cdot}0$ cm., $x_1=11{\cdot}86$ cm. ; or

$$\frac{x_2}{x_1}=\cdot 84.$$

The ratio of specific electrical resistances for these rods was found to be ·95 ; assuming this as the ratio of $k_2$ to $k_1$, we get

$$\frac{x_2}{x_1}=\sqrt{\frac{k_2r_2}{k_1r_1}}=0{\cdot}89,$$

the mean result found by experiment being 0·85.

It is to be noted that there is not so much difference between the radii of the two rods as there was in the other cases.

*Brass Rods,* being the rods previously experimented on.
$x_1=65$ mm. ;
$x_2=47{\cdot}3$ mm. (mean of three determinations).

$$\frac{x_2}{x_1}=\cdot 73,\quad \sqrt{\frac{r_2}{r_1}}=\cdot 87.$$

*Copper Rods,* previously used.
$x_1=60$ mm. ;
$x_2=33$ mm. (mean of three determinations).

$$\frac{x_2}{x_1}=\cdot 55,\quad \sqrt{\frac{r_2}{r_1}}=\cdot 86.$$

*Brass Rods.* These are two new rods, which were used in experiments to be described later.

$$r_1=3{\cdot}21\text{ mm.},\quad r_2=1{\cdot}69\text{ mm.},\quad \sqrt{\frac{r_2}{r_1}}=\cdot 73.$$

As a mean result of a series of experiments, for $x_2=5$ cm., $x_1$ was found to be 7·96 cm. ; or

$$\frac{x_2}{x_1}=\cdot 63$$

It must be pointed out, however, that with the Bunsen burner the parts of the rod nearest the flame become visibly oxidized, this being especially noticeable in the case of the thicker rod—so much so that the increased emissivity so obtained can apparently overcome the greater transmission of heat of the thicker rod. Thus, with the above brass rods, 5 cm. on the thinner rod were found equivalent in this region to 5·2 cm. on the thicker; and after the heating had continued for some time 3·7 cm. on the thicker rod balanced 5 cm. on the thinner one. The ratio given above, ·63, is for parts of the rods that were not oxidized, and did not become so after several days' heating.

The general results obtained so far are :—

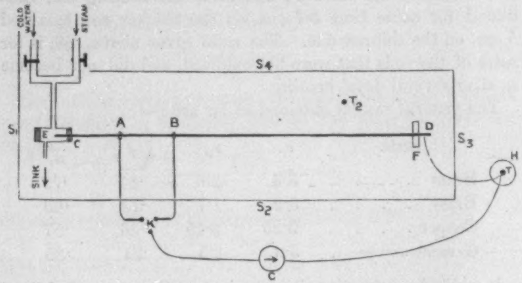
| Rods. | $r_1$. | $r_2$. | $\sqrt{\frac{r_2}{r_1}}$. | $\frac{x_2}{x_1}$. |
|---|---|---|---|---|
| Brass . . . . | 3·4 | 2·6 | ·87 | ·72 |
| Brass . . . . | 3·2 | 1·7 | ·73 | ·63 |
| Copper . . . . | 3·35 | 2·45 | ·86 | ·57 |
| German silver . | 3·0 | 2·5 | ·91 | ·85 |

It will be seen that in every case the rate of fall of temperature along the thinner of the various pairs of rods compared is more rapid than would be inferred according to the usual formula from the distribution of temperature observed along the thicker rod. Consequently this formula cannot be legitimately used for the comparison of conductivities, unless the radii of the rods compared are equal and their surfaces in the same condition.

The only way of escaping from this conclusion is by supposing that the thermal conductivity of the smaller of each pair of rods was less than that of the thicker one. Although it seemed very unlikely that this should be so in the case of every pair, it could not be regarded as impossible. To settle the matter, it was decided to determine the absolute conductivity of at least one pair of rods.

For this purpose Ångström's method was adopted, in which one end of the rod is alternately heated and cooled, and the alternations of temperature observed at two points along the rod. Fig. 1 is a diagram of the apparatus used. C D is the rod, passing into a glass tube E, through which cold water or steam can be passed as desired. E is held up by a clamp, and F is a clamp supporting the rod at the other end, no other clamps being used for the rod. $S_1$, $S_2$, $S_3$, $S_4$ are brown-paper screens, about 2 ft. high, resting on the table and open at the top; $S_3$ is about 1½ ft. wide. A and B are the two points whose temperatures have to be measured.

Fig. 1.

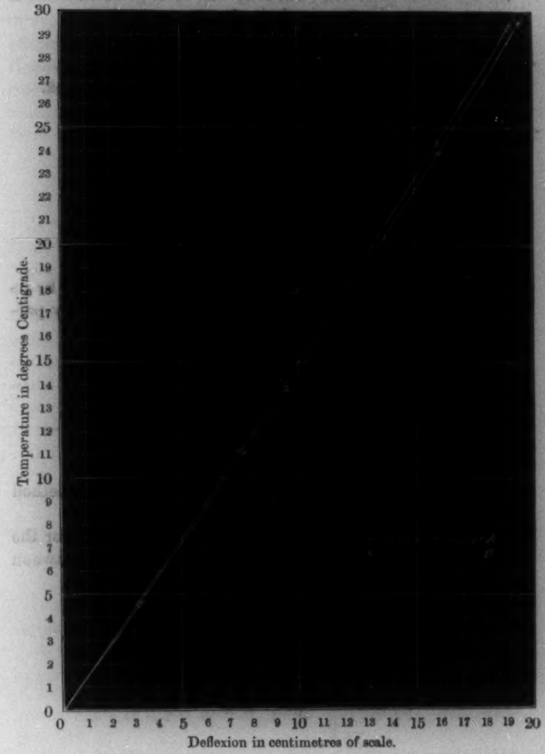


This was done by fine iron wires passing over the rod at the required point, and held down by suitable weights. The wires pass to a key K, through the galvanometer G, to a vessel H containing cold water. H contains the other junction, and a thermometer T. A brass wire connects D to H. $T_2$ is a thermometer reading the temperature of the air. Both thermometers were divided into fifths and read by a telescope.

As it was not possible to keep the temperature of the air constant, allowance had to be made for the change. As the temperature required is the excess of temperature of the rod over the air, this was done by merely subtracting the temperature of the air at the given moment from that of the rod at the same moment.

Experiment showed that it was possible to move the iron wire on the rod, and replace it, and obtain the same reading as previously; thus showing that the resistance of the joint did not appreciably alter. As the galvanometer was made somewhat sensitive, its sensitiveness was tested during the experiments by a Daniell cell passing through a large resist-

Fig. 2.



ance (about 13,000 ohms), the E.M.F. of the Daniell being compared with that of a Clark cell. Zero readings were also taken between each deflexion. The readings of the galvanometer were afterwards standardized, a known difference of temperature being produced between the two junctions, and the deflexions observed. The following table gives an example of a standardization :—

| Point A. | | Point B. | |
|---|---|---|---|
| Diff. of Temp. | Galv. Defl. | Diff. of Temp. | Galv. Defl. |
| 4·56 | 3·10 | 4·62 | 3·18 |
| 11·12 | 7·45 | 11·19 | 7·60 |
| 13·99 | 9·36 | 13·89 | 9·43 |
| 20·29 | 13·37 | 20·34 | 13·67 |
| 24·50 | 16·08 | 23·99 | 16·06 |
| 29·32 | 18·99 | 29·54 | 19·48 |

See fig. 2, which is plotted for these values.

When the temperature of the rod has settled down to its regular cyclic state, the excess of temperature $u$ of any particular point at any instant $t$ may be expressed by

$$u = a + b_1 \sin\left(2\pi\frac{t}{\mathrm{T}} + \beta_1\right) + b_2 \sin\left(4\pi\frac{t}{\mathrm{T}} + \beta_2\right)$$
$$+ b_3 \sin\left(6\pi\frac{t}{\mathrm{T}} + \beta\right) + \ldots,$$

where T is the time-period of the alternations.

The constants $a$, $b_1$, $\beta_1$, &c. are determined by the method of least squares from the observations made.

If $a$, $b_1$, $\beta_1$, &c. and $a'$, $b_1'$, $\beta_1'$, &c. are the constants for the two points A and B respectively, and $x$ the distance between them, then

$$b = b' e^{gx} \quad \text{and} \quad \beta - \beta' = qx$$

(see *Ann. Chim. Phys.* lxvii., 1863).

Hence $g$ and $q$ can be determined, and

$$gq = \frac{n\pi}{\dfrac{k}{c\delta}\mathrm{T}} \quad \text{and} \quad h = (g^2 - q^2)\frac{kr}{2},$$

where $n = 1, 2, 3$, &c., according as you use the constants of the 1st, 2nd, 3rd, &c. sine term ;

$c$ = specific heat of the rod ;

$\delta$ = density of the rod.

Hence *k* and *h* can be determined from each sine term. In the experiments as carried out only the first, and perhaps the third, sine terms are available for these determinations, as the others are very small, the even terms being especially so. Besides these, there is the "*a*" term of the above formula (the constant term of the Fourier series), which is large, and represents the mean excess of temperature of the rod. From this term we get

$$\frac{a}{a'} = e^{x\sqrt{\frac{2h}{kr}}}.$$

If we use the previously determined value of *k*, we can get from this equation a second value of *h*. This will be referred to later on.

The rods experimented upon were three brass rods (commercial specimens) of roughly $\frac{1}{8}$, $\frac{1}{4}$, and $\frac{3}{8}$ in. diameter; their lengths were about 3, 5, and 6 ft. respectively. They were cleaned, but not polished. The time-period of the alternations, and the positions of A and B, were chosen so that the cycle of changes gone through should be as nearly as possible the same in the three cases.

The specific heat was determined by heating a portion of each rod to 100° in a Regnault's apparatus in the usual way. The following are the results obtained :—

| Diam. of Rod .... | $\frac{1}{8}$ in. | $\frac{1}{4}$ in. | $\frac{3}{8}$ in. |
|---|---|---|---|
| | ·0937 | ·0943 | ·0945 |
| | ·0948 | ·0952 | ·0938 |
| | ·0953 | | ·0942 |
| Approx. rise of temp. of calorimeter . . | 0·7 | 1·2 | 1·8 degr. Cent. |

The mean result ·0945 was assumed for all the rods. No correction was made for change of specific heat with temperature.

The following readings are given to show how far they agree for different cycles on the same day :—

| Point A. | | | | Point B. | | | |
|---|---|---|---|---|---|---|---|
| I. Time: $1^{h}\ 0^{m}$. | II. $3^{h}\ 0^{m}$. | III. $4^{h}\ 0^{m}$. | Mean. | I. Time: $1^{h}\ 30^{m}$. | II. $3^{h}\ 30^{m}$. | III. $4^{h}\ 30^{m}$. | Mean. |
| 20·15 | 19·85 | 19·85 | 19·95 | 8·83 | 8·86 | 8·85 | 8·85 |
| 17·16 | 16·93 | 16·91 | 17·00 | 8·88 | 9·00 | 8·99 | 8·96 |
| 13·87 | 13·69 | 13·74 | 13·77 | 8·75 | 8·78 | 8·82 | 8·78 |
| 11·25 | 11·05 | 10·97 | 11·09 | 8·26 | 8·31 | 8·27 | 8·28 |
| ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... |
| 3·16 | 3·05 | 3·06 | 3·09 | 3·86 | 3·94 | 3·88 | 3·89 |
| 2·70 | 2·59 | 2·56 | 2·62 | 3·44 | 3·45 | 3·47 | 3·45 |
| 2·29 | 2·23 | 2·16 | 2·23 | 3·03 | 3·13 | 3·09 | 3·08 |
| 1·97 | 1·88 | 1·83 | 1·89 | 2·66 | 2·78 | 2·75 | 2·73 |

The above readings are deflexions in centimetres : 1 cm. of scale corresponds to a rotation of the magnet through 11′, or 1 cm. corresponds to a difference of temperature between the two junctions of 1½ degrees Cent.

The following expressions show the series required to fit the temperatures obtained; they are the expressions for Set I. of Rod II., but the constants are of approximately the same magnitude with all the rods:—

$$\begin{aligned}\text{Temp. A} = {} & 13{\cdot}95 + 12{\cdot}67 \sin\left(2\pi\frac{t}{T} + 2{\cdot}1412\right) + {\cdot}42 \sin\left(4\pi\frac{t}{T} + 3{\cdot}91\right)\\ & + 2{\cdot}18 \sin\left(6\pi\frac{t}{T} + 1{\cdot}13\right) + {\cdot}18 \sin\left(8\pi\frac{t}{T} + 3{\cdot}33\right)\\ & + {\cdot}80 \sin\left(10\pi\frac{t}{T} + {\cdot}56\right) + \ldots + {\cdot}31 \sin\left(14\pi\frac{t}{T} + {\cdot}28\right).\end{aligned}$$

$$\begin{aligned}\text{Temp. B} = {} & 6{\cdot}16 + 3{\cdot}92 \sin\left(2\pi\frac{t}{T} + 1{\cdot}3806\right) + {\cdot}10 \sin\left(4\pi\frac{t}{T} + 2{\cdot}41\right)\\ & + {\cdot}38 \sin\left(6\pi\frac{t}{T} - {\cdot}40\right) + {\cdot}04 \sin\left(8\pi\frac{t}{T} + 1{\cdot}14\right)\\ & + {\cdot}07 \sin\left(10\pi\frac{t}{T} - 1{\cdot}70\right) + \ldots + {\cdot}03 \sin\left(14\pi\frac{t}{T} - 2{\cdot}68\right).\end{aligned}$$

As an example of the curve of temperatures obtained, see fig. 3. At the abscissa marked 0 min. cold water was turned

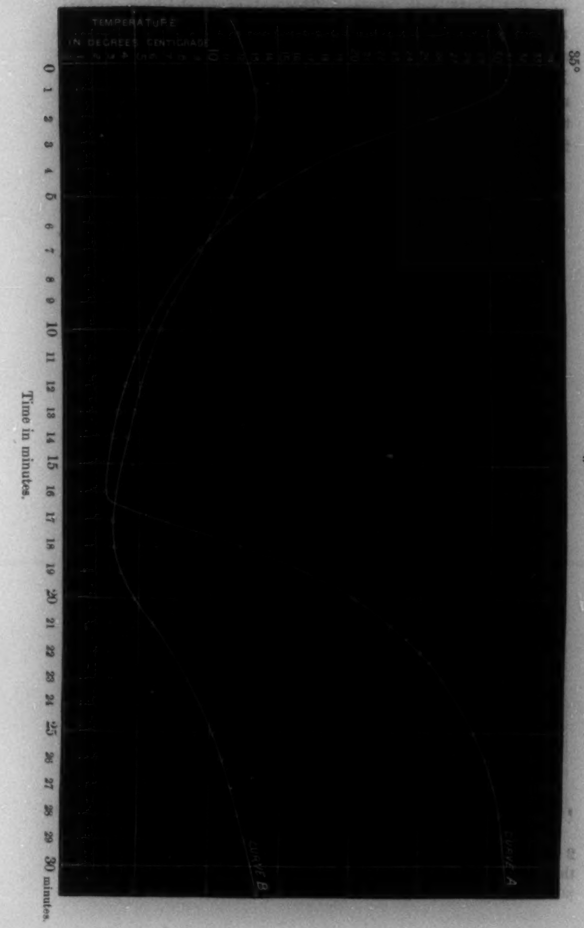

TEMPERATURE
IN DEGREES CENTIGRADE
35°
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30 minutes.
Time in minutes.
CURVE A
CURVE B

Fig. 3.

on, and at 15 min. steam. The points marked are experimental points. There are no points marked at 0 and 15 min. as I had to be in another part of the room at those instants. It will be noticed that the cold water or the steam (as the case may be) has done nearly all it can do, before the other is turned on, especially in the case of A. This can also be seen from the numbers given below.

The following are the details for each rod:—

*Rod* I. (⅛ inch).—Diam. = ·3377 cm. Density = 8·49. Specific electrical resistance = $7 \cdot 24 \times 10^{-6}$ ohms. 7 cms. between junctions. Time-period 10 min. Determination of temperature every half-minute.

| | Set I.* (Mean of 3 cycles.) Excess Temperature in degrees. | | Set II. (Mean of 3 cycles.) Excess Temperature in degrees. | | Set III. (Mean of 4 cycles.) Excess Temperature in degrees. | |
|---|---|---|---|---|---|---|
| Time in mins. | A. | B. | A. | B. | A. | B. |
| 0 | — | — | — | — | — | — |
| ½ | 22·25 | 9·13 | 22·27 | 9·26 | 19·82 | 8·67 |
| 1 | 15·91 | 8·88 | 15·95 | 8·98 | 14·05 | 8·35 |
| 1½ | 10·95 | 7·81 | 11·01 | 7·88 | 9·79 | 7·24 |
| 2 | 7·90 | 6·58 | 7·87 | 6·50 | 6·72 | 6·00 |
| 2½ | 5·67 | 5·29 | 5·68 | 5·29 | 4·83 | 4·71 |
| 3 | 4·35 | 4·35 | 4·27 | 4·29 | 3·42 | 3·79 |
| 3½ | 3·32 | 3·52 | 3·30 | 3·49 | 2·61 | 3·06 |
| 4 | 2·64 | 2·98 | 2·55 | 2·88 | 1·97 | 2·52 |
| 4½ | 2·05 | 2·36 | 2·02 | 2·31 | 1·56 | 2·01 |
| 5 | — | — | — | — | — | — |
| 5½ | 1·80 | 1·78 | 1·43 | 1·60 | 1·10 | 1·48 |
| 6 | 9·11 | 1·65 | 8·63 | 1·56 | 7·46 | 1·42 |
| 6½ | 15·47 | 2·58 | 14·95 | 2·52 | 13·97 | 2·36 |
| 7 | 19·16 | 4·06 | 18·95 | 3·97 | 17·59 | 3·81 |
| 7½ | 20·91 | 5·42 | 20·77 | 5·40 | 19·42 | 5·10 |
| 8 | 22·21 | 6·53 | 22·31 | 6·58 | 20·75 | 6·16 |
| 8½ | 23·08 | 7·41 | 23·31 | 7·42 | 21·65 | 6·99 |
| 9 | 23·69 | 7·95 | 23·96 | 8·16 | 22·49 | 7·65 |
| 9½ | 24·14 | 8·47 | 24·34 | 8·62 | 22·53 | 8·05 |
| Mean Temp. | 27° | 19½° | 27° | 19½° | 27½° | 21° |
| Mean Temp. Air | 14° | | 14° | | 16° | |

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* At the end of this set the joint B was found displaced through about 2 mm. away from A. This introduces a possible error of about 2½ p. c. in the distance, or 5 p. c. in the conductivity, while leaving the emissivity practically unaffected.

The results, in C.G.S. units, calculated from these numbers are :—

| | Set I. | Set II. | Set III. |
|---|---|---|---|
| *Conductivity* (from 1st sine term). | [·2407] | ·2507 | ·2541 |
| *Emissivity*:— | | | |
| From "*a*" term. | ·000321 | ·000331 | ·000319 |
| „ 1st sine term. | ·000397 | ·000403 | ·000405 |

Set II. is probably the best of the three.

*Rod* II. (¼ inch).—Diam.=·6426 cm. Density=8·47. Specific electrical resistance = $7·56 \times 10^{-6}$ ohms. 10 cms. between junctions. Time-period 20 min. Determination of temperature every minute.

| | SET I. (Mean of 4 cycles.) Excess Temperature in degrees. | | SET II. (Mean of 3 cycles.) Excess Temperature in degrees. | |
|---|---|---|---|---|
| Time in mins. | A. | B. | A. | B. |
| 0 | — | — | — | — |
| 1 | 24·12 | 10·29 | 23·67 | 10·13 |
| 2 | 17·60 | 10·07 | 17·33 | 10·02 |
| 3 | 12·66 | 9·15 | 12·62 | 9·09 |
| 4 | 9·23 | 7·80 | 9·34 | 7·91 |
| 5 | 6·88 | 6·54 | 6·95 | 6·69 |
| 6 | 5·23 | 5·40 | 5·46 | 5·60 |
| 7 | 4·01 | 4·52 | 4·27 | 4·68 |
| 8 | 3·18 | 3·76 | 3·33 | 3 91 |
| 9 | 2·43 | 3·13 | 2·60 | 3·30 |
| 10 | — | — | — | — |
| 11 | 2·46 | 2·17 | 2·54 | 2·34 |
| 12 | 9·40 | 2·02 | 9·27 | 2·26 |
| 13 | 15·23 | 2·95 | 14·87 | 3·07 |
| 14 | 19·04 | 4·33 | 18·68 | 4·39 |
| 15 | 21·48 | 5·70 | 21·13 | 5·78 |
| 16 | 23·26 | 6·94 | 22·78 | 6·88 |
| 17 | 24·49 | 7·88 | 23·89 | 7·90 |
| 18 | 25·26 | 8·66 | 24·64 | 8·70 |
| 19 | 25·76 | 9·34 | 25·16 | 9·36 |
| Mean Temp....... | 26¼° | 18¼° | 28° | 20½° |
| Mean Temp. Air. } ...... | 12¼° | | 14¼° | |

Whence by calculation :—

| | Set I. | Set II. |
|---|---|---|
| *Conductivity* (from 1st sine term). | ·2351 | ·2338 |

| *Emissivity* :— | Set I. | Set II. |
|---|---|---|
| From "*a*" term. | ·000253 | ·000236 |
| „ 1st sine term. | ·000301 | ·000286 |

Set II. is the better of the two.

*Rod* III. ($\frac{3}{8}$ inch).—Diam. = ·9654 cm. Density = 8·49. Specific electrical resistance = $7·71 \times 10^{-6}$ ohms. 12 cms. between junctions. Time-period 30 min. Determination of temperature every minute.

| | SET I. (Mean of 3 cycles.) Excess Temperature in degrees. | | SET II. (Mean of 2 cycles.) Excess Temperature in degrees. | | SET III. (Mean of 3 cycles.) Excess Temperature in degrees. | |
|---|---|---|---|---|---|---|
| Time in mins. | A. | B. | A. | B. | A. | B. |
| 0 | — | — | — | — | — | — |
| 1 | 30·85 | 13·15 | 30·83 | 13·21 | 30·15 | 13·02 |
| 2 | 25·96 | 13·32 | 26·20 | 13·38 | 25·59 | 13·18 |
| 3 | 20·86 | 13·05 | 21·15 | 13·14 | 20·57 | 12·92 |
| 4 | 16·75 | 12·35 | 17·09 | 12·45 | 16·54 | 12·19 |
| 5 | 13·52 | 11·36 | 13·91 | 11·47 | 13·41 | 11·19 |
| 6 | 11·19 | 10·31 | 11·51 | 10·41 | 11·04 | 10·15 |
| 7 | 9·28 | 9·27 | 9·55 | 9·34 | 9·11 | 9·15 |
| 8 | 7·80 | 8·27 | 7·96 | 8·34 | 7·62 | 8·15 |
| 9 | 6·57 | 7·32 | 6·74 | 7·45 | 6·37 | 7·26 |
| 10 | 5·63 | 6·51 | 5·66 | 6·63 | 5·35 | 6·51 |
| 11 | 4·80 | 5·77 | 4·81 | 5·85 | 4·50 | 5·72 |
| 12 | 4·10 | 5·17 | 4·11 | 5·17 | 3·81 | 5·06 |
| 13 | 3·60 | 4·64 | 3·55 | 4·60 | 3·25 | 4·49 |
| 14 | 3·11 | 4·12 | 3·07 | 4·12 | 2·75 | 3·97 |
| 15 | — | — | — | — | — | — |
| 16 | 2·65 | 3·34 | 2·44 | 3·28 | 2·16 | 3·19 |
| 17 | 6·67 | 3·07 | 6·59 | 3·03 | 6·29 | 2·92 |
| 18 | 12·19 | 3·21 | 12·28 | 3·15 | 11·91 | 3·03 |
| 19 | 16·75 | 3·87 | 16·85 | 3·81 | 16·44 | 3·67 |
| 20 | 20·23 | 4·93 | 20·25 | 4·88 | 19·79 | 4·71 |
| 21 | 22·83 | 6·10 | 22·81 | 6·03 | 22·40 | 5·85 |
| 22 | 24·87 | 7·24 | 24·85 | 7·17 | 24·39 | 7·08 |
| 23 | 26·45 | 8·28 | 26·43 | 8·25 | 25·97 | 8·07 |
| 24 | 27·70 | 9·21 | 27·56 | 9·17 | 27·13 | 9·08 |
| 25 | 28·68 | 10·03 | 28·44 | 10·04 | 27·90 | 9·89 |
| 26 | 29·55 | 10·82 | 29·22 | 10·76 | 28·69 | 10·62 |
| 27 | 30·10 | 11·37 | 30·04 | 11·30 | 29·25 | 11·24 |
| 28 | 30·56 | 11·91 | 30·31 | 11·84 | 29·80 | 11·75 |
| 29 | 30·97 | 12·37 | 30·77 | 12·35 | 30·17 | 12·19 |
| Mean Temp. | 30° | 21° | 31° | 22° | 31½° | 23° |
| Mean Temp. Air. | 13° | | 14° | | 15° | |

From which by calculation we get:—

| | Set I. | Set II. | Set III. |
|---|---|---|---|
| *Conductivity* (from 1st sine term). | ·2374 | ·2386 | ·2399 |
| *Emissivity*:— | | | |
| From "*a*" term. | ·000208 | ·000208 | ·000205 |
| „ 1st sine term. | ·000251 | ·000237 | ·000237 |

Set I. is the best of the three.

The third sine term is, in the case of B, too small to give reliable results, but they have been calculated in some cases, and curiously enough the conductivity always comes out lower than that given by the first term. The following have been calculated:—

| | Rod I. | | Rod II. | Rod III. | | |
|---|---|---|---|---|---|---|
| | Set II. | Set III. | Set I. | Set I. | Set II. | Set III. |
| *Conductivity*—1st sine term. | ·251 | ·254 | ·235 | ·237 | ·239 | ·240 |
| 3rd „ „ | ·229 | ·242 | ·233 | ·222 | ·229 | ·227 |
| *Emissivity* — 1st sine term. | ·00040 | ·00040 | ·00030 | ·00025 | ·00024 | ·00024 |
| 3rd „ „ | ·00038 | ·00025 | ·00027 | ·00024 | ·00026 | ·00031 |

Taking the mean of the chief results obtained, we get the following table:—

| | Rod I. | Rod II. | Rod III. |
|---|---|---|---|
| *Conductivity* . . . | ·2524 | ·2344 | ·2386 |
| *Emissivity*:— | | | |
| From "*a*" term. | ·000324 | ·000244 | ·000207 |
| „ 1st sine term. | ·000402 | ·000293 | ·000242 |

It hence appears that the emissivity of a body depends to a large extent on the form and dimensions of that body, and that the formula for conduction of heat along a rod, as usually given in text-books, can only be used in a very restricted sense.

It will be noticed that the two emissivities (deduced from the "*a*" term and the sine term) are to one another approximately as 1 to 1·2. The ratio appears to be too uniform to be due to accidental error of experiment, but the meaning of the two values is not quite clear. In order to obtain further information, the ⅝ inch rod was heated at one end by steam under approximately the same conditions as before, and the E.M.F. of a german-silver-iron couple at different points on the rod determined by the compensation method in the ordinary way. A preliminary set was taken, which gave about the same results as the following more accurate set (readings were taken going down the rod and then going up):—

| Position on rod in cm. | Bridge-Reading in cm. | | |
|---|---|---|---|
| | Down. | Up. | Mean. |
| 0 | 73·8 | 73·7 | 73·75 |
| 5 | 53·1 | 52·6 | 52·85 |
| 10 | 38·0 | 38·0 | 38·0 |
| 15 | 27·6 | 27·5 | 27·55 |
| 20 | 19·8 | 20·0 | 19·9 |
| 25 | 14·4 | 14·7 | 14·55 |
| 30 | 10·6 | 10·8 | 10·7 |
| 35 | 7·8 | 7·8 | 7·8 |

Temperature of air about 10½°.

1 cm. of bridge-wire corresponds to rather less than one degree.

Dividing the above into two lots, and taking $k = \cdot 2386$, we get (this method is sufficiently accurate for this purpose):—

| Mean temp. | $h$. |
|---|---|
| 54° | ·000247 |
| 42° | ·000240 |
| 33° | ·000231 |
| 27° | ·000229 |

The mean temperature of the rod in the experiments by Ångström's method was about 27°, and the two emissivities found were ·000207 and ·000242, so that the steady-state emissivity comes just about halfway between the two. The rod, however, had become somewhat tarnished during the summer, and had to be cleaned again, which may or may not have made some difference. Further experiments will be needed to settle the point conclusively.

When the last part of the experiments was in progress, Mr. A. W. Porter, B.Sc., drew my attention to Messrs. Ayrton and Kilgour's paper before the Royal Society on the variation of emissivity with the diameter of the wires experimented upon. The results obtained corroborate one another, and also corroborate results that had been obtained some time ago by Péclet, and which are recorded in his *Traité de la Chaleur*. Péclet appears to have carried out a large number of experiments on emissivity, the best account of which is found in the 3rd edition (not the 4th) in vol. i. and a long note at the end of vol. iii. (published in 1860–61).

In conclusion I must express my obligations to Prof. Foster and Mr. Porter for much help given in the course of these experiments.

## XXXII. *On the Influence of the Dimensions of a Body on the Thermal Emission from its Surface.* *By* ALFRED W. PORTER, *B.Sc., Demonstrator of Physics, University College, London*[*].

IN discussing the rate at which heat passes outwards from a conducting body into the medium in which it is immersed, it is usually assumed that (for small excesses of temperature of the body above its surroundings) it may be taken as proportional to the excess of temperature. This law is followed, as far as is known, if the body is in a vacuum and loses heat simply by radiation between its own and surrounding surfaces. If, however, it is immersed in a medium, such as air, which carries away heat by conduction and convection as well as by radiation, the problem becomes more complicated, and to assume that the whole effect may be treated as radiation only does not give results which are even an approximation to those obtained experimentally. For example, on this assumption the amount passing outwards from unit area of the surface per second per unit excess of temperature (*i. e.* the "emissivity") should be independent of the size of the body. Results obtained by Péclet from experiments on cylinders and spheres of different sizes show that this constant depends materially upon the sizes of the bodies experimented upon. Péclet's formulæ connecting the rate of emission (exclusive of the radiation effect) with the radius ($r$) for 0° C. excess are:—

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[*] Read January 11, 1895.

For a horizontal infinitely long cylinder of brass . . . . $\Big\}$ $2{\cdot}058+\dfrac{{\cdot}0382}{r}$

For a sphere . . . . . . . $1{\cdot}774+\dfrac{{\cdot}13}{r}$

in which kilogrammes, metres, hours are the units employed. Other formulæ are given by him which it is unnecessary to quote here.

These results do not seem to have attracted much notice, as they are not given in any of the text-books of Physics. They do, however, appear in a book compiled for practical men by Box *, from which the formula for the sphere is quoted, on Professor Ayrton's authority, in Everett's 'Illustrations of the C.G.S. System of Units' (1891 edition, p. 133) †.

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* 'A Practical Treatise on Heat for the use of Engineers and Architects,' by Thomas Box. (London, E. and F. N. Spon, 2nd edition, 1876.) This book does not appear to be generally known to physicists; and, judging from recent references to it, I gather that still less is it realized that the author's data are to a great extent obtained from Péclet, although he states the source to which he is indebted in his preface.

† A mistake occurs in Everett as well as in a paper on the same subject published later by Professor Ayrton and Mr. Kilgour in the Phil. Trans. for 1892, in which Everett's statement is quoted. The formulæ are given in Box as

$$\cdot 421+\frac{\cdot 307}{r} \text{ for the cylinder}$$

and

$$\cdot 3634+\frac{1{\cdot}0476}{r} \text{ for the sphere,}$$

in which the units are the pound, foot, and hour, *the radius being however in inches.*

Translated into C.G.S. units, they become

$$\text{Cylinder: } \left[\cdot 572+\frac{1{\cdot}061}{r}\right]\times 10^{-4},$$

$$\text{Sphere: } \cdot 00004928+\frac{\cdot 0003609}{r}.$$

Experiments on thin wires by Messrs. Ayrton and Kilgour have confirmed the fact that the emissivity can be expressed empirically through a considerable range of radius in the form given by Péclet; and experiments on rods which have been in progress in this Laboratory since 1891, an account of which was read by Mr. Eumorfopoulos before the Physical Society on the same day as this paper, lead to the same conclusion.

It was these that first called my attention to the subject; and in order to account approximately for them and the results elsewhere obtained, I propose here to examine the results of supposing the loss to only in part follow the law of radiation, the remainder being assumed to follow the law of conduction.

The rate of loss due to radiation will be proportional to the excess of the temperature of the body above that of its enclosure, and if we reckon temperatures from that of the enclosure, we may write the rate due to this cause

$$h\theta_a,$$

where $h$ is the radiation-constant and $\theta_a$ is the temperature at the surface of the body.

The remainder, which is to include both true conductive and also convective loss, will be proportional to the temperature-gradient in the medium close to the surface of the body. It may on this assumption be represented by

$$-c\left.\overline{\frac{d\theta}{dr}}\right|_a,$$

where $\left.\overline{\frac{d\theta}{dr}}\right|_a$ is the temperature-gradient in the medium at the bounding surface of the body, and $c$ is a positive constant which will be referred to as the convection-conductivity.

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In Everett, and in Ayrton and Kilgour's paper, the latter appears as

$$\cdot 0004928 + \frac{\cdot 0003609}{r}.$$

Further, it is not clear from Everett whether the formula he gives refers to air-effect *plus* radiation or to one of these alone. The specification of "blackened sphere" would lead one to suppose that either the total effect or else the radiation only is meant, since the air-effect has been shown to be independent of the *nature* of the surface. On reference to Péclet, the formula is seen to represent the *air-effect alone*.

The total rate of loss is hence

$$h\theta_a - c\left.\frac{d\theta}{dr}\right|_a,$$

which may be written

$$\left[h - c\frac{\left.\frac{d\theta}{dr}\right|_a}{\theta_a}\right]\theta_a.$$

The expression inside the brackets is the quantity called the "emissivity" in the usual treatment of the problem. On the above assumption, far from being a constant, it is seen to be a thing whose value will vary with every modification of the experiment by which it is sought to be determined.

To fix ideas, take the case of a cylindrical rod or wire of radius "$a$" heated uniformly at all points and maintained at constant temperature by mechanism the nature of which is of no consequence. Let it be surrounded by a coaxal cylindrical sheath of radius R maintained at a constant temperature, which will be taken as the zero of temperature, the intervening space being filled with conducting or pseudo-conducting material. The differential equation to be satisfied by the temperature in the medium is

$$\frac{d^2\theta}{dr^2} + \frac{1}{r}\frac{d\theta}{dr} = 0,$$

since with the above conditions everything is symmetrical with regard to, and uniform parallel to, the axis of the cylinder; and the solution of this which satisfies the boundary conditions is

$$\theta = \theta_a\frac{\log \mathrm{R} - \log r}{\log \mathrm{R} - \log a};$$

whence the emissivity ($e$) becomes

$$h + \frac{c}{a(\log \mathrm{R} - \log a)},$$

or for convenience of calculation,

$$h + \frac{b}{a(\log_{10} \mathrm{R} - \log_{10} a)}.$$

This, then, is presumably an approximation to a theoretic formula for the case of experiments like those of Messrs. Ayrton and Kilgour referred to before; and the accompanying Table I. and curves (fig. 1) (pp. 348 & 349) show how closely, by a suitable choice of constants, it can represent the experimental values. The constants I determined by the method of least squares; this I considered it advisable to do, because the experimental values are not sufficiently precise to enable one to draw a smooth curve through them with anything like certainty. In particular I may mention that their own empirical formulæ fail to fit in with the experimental values yielded by the wire of radius ·0037; and these values are similarly shunned by the formulæ which I give.

The first term in each of my formulæ should represent the radiation-constant. It must be noted, however, that for such very thin wires radiation forms only a small portion of the whole emission; and therefore, without having results of greater accuracy from which to deduce the formulæ, it is not possible to assign the value of this term with definiteness. All the values for it are, however, higher than those obtained by observers who have experimented on the emission from surfaces *in vacuo*, as the following data show:—

*Radiation Values.*

| | | | |
|---|---|---|---|
| Quoted from Everett. | Bottomley: Sooted globe in Sprengel vacuum ............ | ·000125 for excess of | 83°·6. |
| | | ·000095 „ „ | 32°·7. |
| | Bottomley: Silvered and highly polished globe ............ | ·0000354 „ „ | 72°·1. |
| | | ·0000296 „ „ | 43°·7. |
| | Nichol (published by Tait): Pressure of air = 10 mm. of mercury ......... | ·000057 „ „ | 42°. |

As regards the other constant "$b$" ($=\cdot 4343\,c$), we have

At 300° . . $b=\cdot 0696\times 10^{-3}$, $c=\cdot 16\ \times 10^{-3}$,
200° . . $b=\cdot 0620\times 10^{-3}$, $c=\cdot 143\times 10^{-3}$,
150° . . $b=\cdot 0605\times 10^{-3}$, $c=\cdot 139\times 10^{-3}$,
100° . . $b=\cdot 0549\times 10^{-3}$, $c=\cdot 126\times 10^{-3}$.

Péclet's results were derived from experiments on five cylinders: only two of them are available for my purpose, since the others were either of different material or different surface. They were short cylinders of unpolished brass, terminated by hemispherical ends, allowance for which was

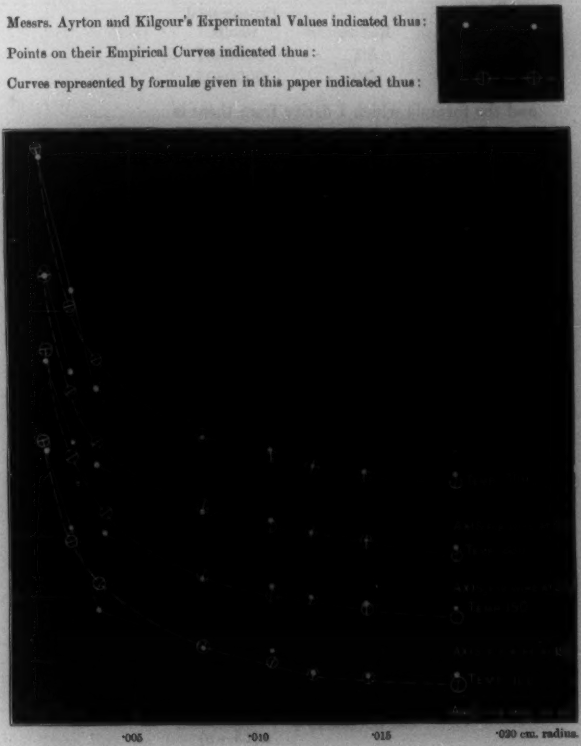
TABLE I.—Thermal Emissivities of Wires at different Temperatures obtained experimentally by Messrs. Ayrton and Kilgour, compared with calculated Values.

| $a$. Radius of wire, in centimetres. | Temperature 300°. | | | Temperature 200°. | | | Temperature 150°. | | Temperature 100°. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Experimental values $\times 10^3$. | Values calculated from | | Experimental values $\times 10^3$. | Values calculated from | | Experimental values $\times 10^3$. | Values calculated from formula given in this paper. | Experimental values $\times 10^3$. | Values calculated from | |
| | | Ayrton and Kilgour's formula. | Formula given in this paper. | | Ayrton and Kilgour's formula. | Formula given in this paper. | | | | Ayrton and Kilgour's formula. | Formula given in this paper. |
| ·00155 | 14·40 | 14·54 | 14·69 | 12·78 | 13·03 | 12·80 | 11·87 | 12·30 | 10·85 | 11·04 | 11·22 |
| ·00255 | 9·85 | 9·18 | 9·39 | 9·07 | 8·26 | 8·47 | 8·60 | 8·07 | 7·90 | 7·07 | 7·38 |
| ·00370 | 5·84 | 6·68 | 6·92 | 5·38 | 6·04 | 6·27 | 5·09 | 5·92 | 4·55 | 5·20 | 5·43 |
| ·0076 | 3·84 | 3·82 | 3·92 | 3·46 | 3·49 | 3·59 | 3·21 | 3·31 | 2·93 | 3·05 | 3·06 |
| ·0103 | 3·35 | 3·12 | 3·12 | 3·08 | 2·88 | 2·88 | 2·94 | 2·61 | 2·80 | 2·53 | 2·43 |
| ·0118 | 2·84 | 2·86 | 2·83 | 2·59 | 2·65 | 2·61 | 2·45 | 2·36 | 2·30 | 2·33 | 2·19 |
| ·0141 | 2·61 | 2·58 | 2·48 | 2·36 | 2·40 | 2·31 | 2·22 | 2·06 | 2·05 | 2·12 | 1·93 |
| ·0178 | 2·29 | 2·28 | 2·11 | 2·14 | 2·13 | 1·96 | 2·03 | 1·73 | 1·89 | 1·90 | 1·63 |
| | Formulæ referred to above.<br>Ayrton and Kilgour's:—<br>$e = \cdot 001135 + \frac{\cdot 016084}{D}$,<br>where D is diameter in mils.<br>Formula from which the last column is calculated:—<br>$e = \left[\cdot 29 + \frac{\cdot 0696}{a \log\left(\frac{2 \cdot 54}{a}\right)}\right] \times 10^{-3}$. | | | Formulæ referred to above.<br>Ayrton and Kilgour's:—<br>$e = \cdot 001111 + \frac{\cdot 014303}{D}$,<br>where D is diameter in mils.<br>Formula from which the last column is calculated:—<br>$e = \left[\cdot 36 + \frac{\cdot 0620}{a \log\left(\frac{2 \cdot 54}{a}\right)}\right] \times 10^{-3}$. | | | No formula given by Ayrton and Kilgour.<br>Formula from which the second column is calculated:—<br>$e = \left[\cdot 16 + \frac{\cdot 0605}{a \log\left(\frac{2 \cdot 54}{a}\right)}\right] \times 10^{-3}$. | | Formulæ referred to above.<br>Ayrton and Kilgour's:—<br>$e = \cdot 001036 + \frac{\cdot 012078}{D}$,<br>where D is diameter in mils.<br>Formula from which the last column is calculated:—<br>$e = \left[\cdot 20 + \frac{\cdot 0549}{a \log\left(\frac{2 \cdot 54}{a}\right)}\right] \times 10^{-3}$. | | |

Fig. 1.

Thermal Emissivities of Wires at Different Temperatures.

Ordinates represent Emissivities.
Abscissæ represent Radii of Wires.



Messrs. Ayrton and Kilgour's Experimental Values indicated thus:

Points on their Empirical Curves indicated thus:

Curves represented by formulæ given in this paper indicated thus:

made from the experiments on spheres. Péclet, therefore, considered his results to apply to infinitely long cylinders. Their radii were 5·1 and 6·9 cm. respectively, and measurements were made on them in a cylindrical enclosure 40 cm. radius and 100 cm. long. His results are :—

| Radius. | Experimental results. |
|---|---|
| 5·1 | ·0000867 |
| 6·9 | ·0000803 |

and the formula which I derive from these is

$$e = \cdot0000383 + \frac{\cdot00022}{a(\log_{10} 40 - \log_{10} a)}.$$

In large cylinders like these radiation plays a more conspicuous part, and the value of the first term in my formula which represents it is in very good accordance with values obtained by direct methods. The value of "$b$" is, however, very different from that obtained from Ayrton and Kilgour's experiments; and the conclusion is forced upon one that although to consider "$b$" a constant may serve as long as the enclosure remains the same, it will by no means suffice to take it the same constant under such widely different conditions as obtain in these two sets of experiments. The character of the convective flow is evidently totally different in the two cases.

The same conclusion is arrived at by an examination of results obtained from experiments on spheres. The formula for a sphere, found by means of the same assumption as before, is

$$e = h + \frac{cR}{a(R-a)}.$$

Péclet experimented on three spheres in the same enclosure; and assuming the enclosure to behave like a spherical one of 45 centim. radius, the formula becomes

$$e = \cdot00003845 + \frac{\cdot000417 \times 45}{a(45-a)}.$$

The experimental and calculated values are here given:—

| Radius in centim. | Experimental value of $c$ for 0° excess. | Calculated value from above formula. | Calculated by Péclet's own formula for air-effect and adding radiation. |
|---|---|---|---|
| 7·465 | ·0001051 | ·0001054 | ·0001048 |
| 10·58 | ·0000898 | 899 | 906 |
| 15·38 | ·0000801 | 796 | 800 |

It will be observed that the radiation-constant is practically the same as that derived from his cylinder results*, while the value of $c$ is rather less.

Experiments on spheres (both of 2 centim. radius) have also been made by MacFarlane† and extended by Bottomley‡, both using the same enclosure, which was of "large dimensions" (*Bottomley*).

Extrapolation from Péclet's results for a sphere of 2 centim. radius in his enclosure gives :—

| Using his formula. | Using formula given above. |
|---|---|
| ·000237. | ·000256 |

MacFarlane's results for a blackened sphere (Péclet's were dull) give ·000238 for 0° excess. Bottomley's results give about ·000260 for 0° excess, showing that the formula derived from Péclet's results is roughly applicable here.

Bottomley also experimented on the same sphere in a spherical enclosure of 5 centim. radius. If the formulæ hitherto given in this paper were applicable to this case, the emissivity ought to increase with decrease of radius of enclosure. Bottomley's results show a marked *decrease*. The value at 17° for 0° excess is not more than ·00011 after correcting approximately for temperature.

---

* Péclet endeavoured to estimate the radiation independently by means of a thermopile, and deducted it from the total emission to obtain the air-effect. The value he obtained was only ·0000072 for 0° excess, a value so much smaller than received values that I have ignored it entirely, and dealt only with the total effect.

† D. MacFarlane, Proc. Roy. Soc. 1892.

‡ J. T. Bottomley "On Thermal Radiation in Absolute Measure," Trans. Roy. Soc. 1892.

Since the true radiation was determined separately it is possible to find the value of "*c*" for these experiments, although only one sphere was employed. I subjoin a table:—

| From | *c*. |
|---|---|
| Péclet's results from spheres ......... | ·000417. |
| MacFarlane's and Bottomley's results in *large* enclosure, assuming Bottomley's value for radiation ... | about ·0004. |
| Bottomley's results for sooted sphere in small enclosure .................. | ·000192 for excess of 85° C. |
| | 181 ,, ,, 65° C. |
| | 168 ,, ,, 45° C. |
| | 160 ,, ,, 35° C. |
| Bottomley's results for silvered and highly polished sphere in small enclosure .............................. | ·000168 for excess of 65° C. |

Place against these the values obtained from cylinders:—

| From | *c*. |
|---|---|
| Péclet's results in large enclosure ... | ·000508 for 0° excess. |
| Ayrton and Kilgour's, in enclosure of 2·54 centim. radius ............... | ·000160 with wire at 300° C. |
| | 143 ,, ,, 200° C. |
| | 139 ,, ,, 150° C. |
| | 126 ,, ,, 100° C. |

In order to throw light on this question, I have started experiments, in conjunction with Mr. Eumorfopoulos, on cylindrical rods in cylindrical enclosures of different radii. Experiments made so far are as follows:—

A brass rod ·483 centim. radius has soldered on it *two* thermoelectric junctions of iron and german-silver at a distance apart of 10 centim., each of which is part of a couple whose other junction is kept cold in a water-pot. The rod is heated at one end by steam until the steady state of temperature is attained, and the ratio of the temperatures (reckoning from enclosure temperature as zero) of the two junctions is measured successively with different water-jackets embracing the rod.

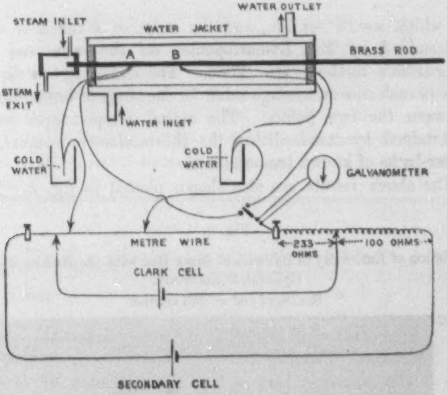
The general arrangement is shown in fig. 2 (p. 353).

Tap-water is passed through the water-jacket at such a rate that its temperature as it enters is sensibly the same as when it leaves the jacket. This temperature is read by a thermometer, as also are the temperatures of the cold junctions. Then either the junction at A and its corresponding cold junction, or the junction at B and its corresponding cold junction, can be connected to a potentiometer, and the thermoelectric E.M.F. in each case determined.

The potentiometer was standardized from time to time by a Clark's cell which is so connected (switches not shown) that the same galvanometer does for all three operations.

The ratio of the thermoelectric E.M.F.'s is approximately the same as the ratio of the excess temperatures of the points

Fig. 2.



A and B after it has been corrected for slight differences of temperature between the two water-baths and the water-jacket. Two jackets have been employed so far, and compared with each other and with the bar unjacketed. In this last case the bar is merely shielded from the ruder form of draught by brown-paper screens.

The results are given in the subjoined table:—

| R. Inner radius of enclosure in centim. | Excess temperature of A. $\theta_A$. | Excess temperature of B. $\theta_B$. | Average excess. | Emissivity at stated mean excess temperature. | Emissivity approximately corrected to one temperature. |
|---|---|---|---|---|---|
| Indefinitely great. | 54·0 | 30·5 | 42·2 | ·0001882 | ·000191 |
| 5·15 | 57·0 | 33·6 | 45·3 | ·0001610 | ·000162 |
| 1·6 | 61·1 | 36·6 | 48·8 | ·0001514 | ·000151 |

The values of emissivity here given have been calculated from the formula

$$e = \frac{kr}{2}\left[\frac{\log\theta_A - \log\theta_B}{\cdot 4343 \times x}\right],$$

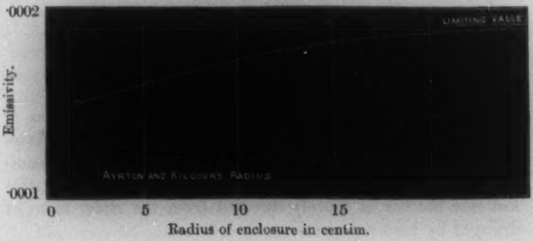
in which $x=10$ centim., and the value of $k$ taken is that determined by Mr. Eumorfopoulos for the same rod by Ångström's method, viz. ·2386. The emissivity is therefore in each case an average value for the range of temperature between the two points. The actual temperatures were ascertained by standardizing the thermoelectric couples in water-baths of known temperatures.

The above results are also shown plotted in fig. 3. An

Fig. 3.

Variation of Emissivity of Cylindrical Brass Rod with the Radius of its Cylindrical Enclosure.

Radius of rod = ·483 centim.



elastic curve (bent steel lath) has been made to pass through the two results for definite dimensions and extended provisionally by a dotted line so as to rise asymptotically to the highest value. It is unsafe to rest too much upon these few results : more will need to be obtained before the law of variation can be stated with certainty : the following paragraph must be considered therefore as merely provisional. Take the two definite values and also (by *inter*polation) the value for an enclosure of 2·54 centim. radius (that employed by Messrs. Ayrton and Kilgour) and find the values of "*b*." They are :—

| Radius of enclosure. R. | Radius of rod. *a*. | *b*. |
|---|---|---|
| 1·6 | ·483 | $\cdot 029 \times 10^{-3}$ |
| 2·54 | ·483 | ·0418 „ |
| 5·15 | ·483 | ·0643 „ |

The value derived from A. and K.'s results at 60° is $\cdot 047 \times 10^{-3}$. As their thin wires blocked up the enclosure less than the thick rod here employed, it is natural that the value obtained from them should be greater than that given above.

The formula which I have given for a cylinder appears to hold through a far wider range than that given by Messrs. Ayrton and Kilgour. Take for example their formula for a wire at 100°. The emissivity for it can never (for any radius) fall lower than

$$\cdot 00107.$$

Calculating from my formula we get

$$\cdot 00036$$

for a rod of ·483 centim. radius at 100°. On reduction to 60° it becomes about

$$\cdot 00025,$$

which is much more within sight of the value ·000154 which is obtained from fig. 3. Considering the violent nature of the extrapolation here made, the agreement is probably as close as could reasonably be expected.

### *Conclusions.*

i. That the theoretic assumption made in this paper gives results which are accordant through a wide range of radius of rod with experimental results obtained under similar conditions as regards enclosure: and in this respect is far superior to the usual assumption which gives no account whatever of variation of the value of emissivity with radius.

ii. That if the freedom permitted to convection effects be varied, as it will be if the enclosure be changed, it is necessary to consider the convecto-conduction constant as varying with the changed conditions according to a law which can only be found by a complete series of experiments made with enclosures of different dimensions.

iii. I conclude that the enclosing boundary is as important a factor in determining the value of the emissivity as the size of the body itself: and that therefore in any collection of data (such as Everett's) it is very necessary to specify the exact nature of the enclosure in which the experiments were conducted; and, further, that all determinations that have been made of this constant and published with imperfect description of all the boundaries are of little scientific value.

Finally, I must express my thanks to Prof. G. C. Foster for kindly advice and suggestions given from time to time in connexion with this matter.

### DISCUSSION.

Prof. CAREY FOSTER thought that in demonstrating the influence of the enclosure Mr. Porter had established an important point.

Prof. AYRTON agreed as to the importance of the influence of the enclosure. Some years ago he had noticed that when the diameter of a wire was small, the power required to keep it red-hot by the passage of a current was nearly independent of the diameter. This would also follow from Péclet's formula. He urged that in such experiments as those of Mr. Porter and Mr. Eumorfopoulos, the conductivity and emissivity, which were functions of the temperature, should not be assumed constant along the bar.

Mr. **Trotter** objected to the use of the term emissivity as including loss of heat by contact with the air, in addition to the loss by radiation.

Mr. **Griffiths** said that in some of his experiments, where a wire conveying an electric current was immersed in a liquid in order to heat the latter, the rise of the temperature of the wire above that of the liquid was found to be nearly independent of the diameter of the wire.

Mr. **Eumorfopoulos**, replying to Prof. Ayrton's criticism, said that in each case his comparison had been between portions of bars in which the range of temperature was the same. Moreover, the variation of the emissivity and conductivity with temperature, as found by other observers, would be quite insufficient to account for his results.

Mr. **Porter** said that the term emissivity had come to be accepted as referring to all heat lost at the surface of a body, whether by radiation or by conduction and convection. In that sense he had used the term.

Prof. **Rücker** thought that emissivity, in this sense, was not a good term, but to change now would probably only make greater confusion.

## XXXIII. *On the Passage of an Oscillator Wave-train through a Plate of Conducting Dielectric.* *By* GEORGE UDNY YULE, *Demonstrator in Applied Mathematics, University College, London.*

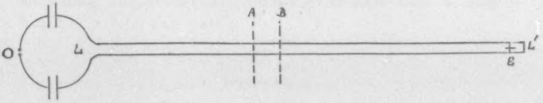
I. Introduction.
II. The Phenomena at the First Surface of the Plate.
III. The Phenomena at the Second Surface of the Plate.
IV. The Intensity of the Transmitted Ray.
V. The Intensity of the Reflected Ray.
VI. Discussion of an Experimental Case and a Correction.
VII. The Numerical Value of some of the previous Results.
Synopsis of Symbols.

### I. *Introduction.*

THE problem treated in these pages was suggested by the following experimental results, for a fuller account of which I may refer to a previous paper †.

A series of wave-trains generated by an oscillator O were allowed to propagate themselves along a double-wire circuit LL′ about 100 metres in length. At the middle of the circuit the wires were run through a jar containing a certain depth AB of distilled water, alcohol, or a very dilute electrolyte.

Fig. 1.



The intensity of the ray transmitted by this slightly absorbent layer was determined by an electrometer E placed at a quarter wave-length (2·25 metres) from the closed end of the circuit. This intensity varied periodically with the thickness of the layer, as in the analogous case of a ray of light and a "thin plate."

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* Read January 11, 1895.

† Phil. Mag. vol. xxxvi. p. 531, Dec. 1893. Prelim. Paper in the Proc. Roy. Soc. vol. liv. p. 96. A sketch of an approximate theory was given in the Phil. Mag. paper, but several assumptions there made were unjustifiable.

The layer AB was what Boltzmann has termed a "conducting dielectric," *i. e.* both its conducting and dielectric properties were of importance. The theory of a non-conducting plate is much simpler: a problem equivalent to it has recently been treated by Dr. E. H. Barton *, to whose work I shall have several occasions to refer. In the more complex problem I have assumed, we have simply a plane-fronted damped wave-train travelling through an insulating medium and falling at normal incidence on an infinite slab of conducting dielectric. The magnetic permeability of both the plate and the surrounding medium are taken as unity.

The theoretical transmission-curve obtained on these assumptions does not agree well with the experimental one, the divergence being the same in sign and order of magnitude as that noticed by Dr. Barton in his case. We have in fact idealized the experimental facts too far in endeavouring to simplify the analysis: the electrolyte was not at all infinite in extent, and at least one important correction is obviously necessary (section VI.). The experiments can only be regarded as a very rough illustration of the problem, and as giving the *raison d'être* of this paper.

The general results obtained seem to be of considerable interest. The intensities of the reflected rays, the phase-changes, and so on, for damped wave-trains reflected from such a plate differ from those for steady rays in some cases very considerably.

For convenience and brevity, the surrounding medium is hereinafter generally referred to as "the dielectric," and the conducting slab as "the plate" or "electrolyte."

## II. *The Phenomena at the First Surface of the Plate.*

In this section we will deal with the phenomena occurring at the first surface of the "electrolyte" only.

The direction of propagation of the ray is chosen as the positive direction of the axis of $z$ and the origin is taken indefinitely close to the interface.

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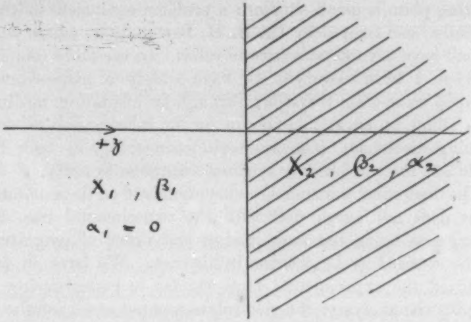
* Preliminary Paper, Proc. Roy. Soc. vol. liv. p. 85; more fully in Thesis for the D.Sc. London, 1894, or Wied. *Ann.* vol. liii. p. 513, 1894. Final paper, Proc. Roy. Soc., read April 1893 (not yet published).

The suffix 1 always refers to the dielectric and the suffix 2 to the plate.

Fig. 2.



Let $X_1$ be the electric force in the dielectric and $X_2$ that in the plate. Under the limitations we have set ourselves—plane waves and non-conducting dielectric—Maxwell's equations assume the simple forms

$$\beta_1 \frac{d^2 X_1}{dt^2} = \frac{d^2 X_1}{dz^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\left(\alpha_2 + \beta_2 \frac{d}{dt}\right) \frac{dX_2}{dt} = \frac{d^2 X_2}{dz^2}, \quad . \quad . \quad . \quad . \quad (2)$$

where we have abbreviated Maxwell's notation by putting

$$\beta_1 = \mu_1 \kappa_1, \quad \beta_2 = \mu_2 \kappa_2, \quad \alpha_2 = 4\pi \mu_2 C_2, \quad . \quad . \quad (3)$$

$\mu_2$ being the magnetic permeability of the plate, $\kappa_2$ its dielectric constant, $C_2$ its conductivity; $\mu_1$ $\kappa_1$ are the same constants referring to the dielectric, $C_1$ being zero. As already stated, we will only take the case of both media being non-magnetic, or

$$\mu_2 = \mu_1 = 1.$$

As a solution of equations (1) and (2) we select

$$\left.\begin{aligned} X_1 &= A_1 e^{p(t - \sqrt{\beta_1} z)} + A_1' e^{p(t - \sqrt{\beta_1} z)} \\ X_2 &= B_2 e^{p(t - qz)} \end{aligned}\right\} \quad . \quad . \quad (4)$$

where $t$ must be not less than zero. $p$ is either wholly imaginary or complex according as the incident ray is steady or damped: $q$ is as yet undetermined; $A_1$ is the amplitude of the incident wave-train, $A_1'$ of the reflected wave-train, and $B_2$ of the transmitted wave-train.

Inserting the value of $X_2$ given in (4) in equation (2), and carrying out the differentiation, we get

$$q = \sqrt{\beta_2}\left(1 + \frac{\alpha_2}{\beta_2 p}\right)^{\frac{1}{2}}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

so $q$ is also partly imaginary.

To determine $\frac{A_1'}{A_1}$ and $\frac{B_2}{A_1}$ we require another pair of equations. These will be given us by the interface conditions: the conditions namely, that there must be no discontinuous jump in the values of either the tangential electric force or the tangential magnetic force, at any time, in passing from the dielectric to the electrolyte. That is, we must have

$$\left.\begin{array}{c} X_1 = X_2, \\ \dfrac{dX_1}{dz} = \dfrac{dX_2}{dz}, \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where

$$z=0, \quad t=\text{anything}.$$

Inserting the values of $X_1$ and $X_2$ in (6) we get, putting $z=0$,

$$\left.\begin{array}{c} A_1 + A_1' = B_2, \\ p\sqrt{\beta_1}\,(-A_1 + A_1') = -pqB_2; \end{array}\right\} \quad . \quad . \quad . \quad (7)$$

and solving these two equations for $\frac{A_1'}{A_1}$, $\frac{B_2}{A_1}$,

$$\frac{A_1'}{A_1} = -\frac{\dfrac{q}{\sqrt{\beta_1}} - 1}{\dfrac{q}{\sqrt{\beta_1}} + 1},$$

$$\frac{B_2}{A_1} = \frac{2\sqrt{\beta_1}}{\sqrt{\beta_1} + q}.$$

If we write for brevity

$$\left.\begin{aligned}\lambda&=\frac{\sqrt{\beta_1}}{q},\\ \frac{A_1'}{A_1}&=-\frac{1-\lambda}{1+\lambda},\\ \frac{B_2}{A_1}&=\frac{2\lambda}{1+\lambda},\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$\lambda$ contains $q$, which is partly imaginary; so we must separate the real and imaginary quantities and rationalize. Let $p_1$ be the real part of $p$, and $p_2$ the imaginary part, so that

$$p=-p_1+p_2 i,$$

and let us write

$$\left.\begin{aligned}p_1&=\eta\cos\chi,\\ p_2&=\eta\sin\chi.\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

In this notation then

$$\left.\begin{aligned}p&=-\eta e^{-i\chi},\\ \text{period}&=\frac{2\pi}{p_2},\\ \text{logarithmic decrement}&=\frac{2\pi p_1}{p_2};\end{aligned}\right\}$$

and using the value of $q$ in (5),

$$\lambda=\sqrt{\frac{\beta_1}{\beta_2}}\frac{1}{\left(1-\frac{\alpha_2}{\eta\beta_2}e^{i\chi}\right)^{\frac{1}{2}}}.$$

The denominator of this expression is

$$\left(1-\frac{\alpha_2}{\eta\beta_2}\cos\chi-i\frac{\alpha_2}{\eta\beta_2}\sin\chi\right)^{\frac{1}{2}},$$

so if we put

$$\left.\begin{aligned}\rho\cos\theta&=1-\frac{\alpha_2}{\eta\beta_2}\cos\chi\\ \rho\sin\theta&=\frac{\alpha_2}{\eta\beta_2}\sin\chi\end{aligned}\right\}, \quad . \quad . \quad . \quad (10)$$

or

$$\rho=\left[1-\frac{\alpha_2}{p_2\beta_2}\sin 2\chi+\left(\frac{\alpha_2}{p_2\beta_2}\sin\chi\right)^2\right]^{\frac{1}{2}}$$

$$\tan\theta=\frac{\frac{\alpha_2}{p_2\beta_2}\sin^2\chi}{1-\frac{1}{2}\frac{\alpha_2}{p_2\beta_2}\sin 2\chi},$$

the denominator becomes $\rho e^{-\frac{i\theta}{2}}$. Writing

$$r=\sqrt{\frac{\beta_1}{\beta_2}}\,\frac{1}{\sqrt{\rho}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

as a further abbreviation we have

$$\lambda=re^{\frac{i\theta}{2}}.$$

We can now proceed to rationalize the values of $\frac{A_1'}{A_1}$ and $\frac{B_2}{A_1}$ given in (8). Inserting our value of $\lambda$,

$$\frac{A_1'}{A_1}=-\frac{1-re^{\frac{i\theta}{2}}}{1+re^{\frac{i\theta}{2}}}=-\frac{1-r\cos\frac{\theta}{2}-ir\sin\frac{\theta}{2}}{1+r\cos\frac{\theta}{2}+ir\sin\frac{\theta}{2}}.$$

Multiplying numerator and denominator by

$$1+r\cos\frac{\theta}{2}-ir\sin\frac{\theta}{2},$$

this becomes

$$-\frac{1-r^2-2ir\sin\frac{\theta}{2}}{1+r^2+2r\cos\frac{\theta}{2}},$$

and multiplying again by $1-r^2+2ir\sin\frac{\theta}{2}$,

$$\frac{A_1'}{A_1}=-\frac{1+r^4-2r^2\cos\theta}{\left(1+r^2+2r\cos\frac{\theta}{2}\right)\left(1-r^2+2ir\sin\frac{\theta}{2}\right)}.$$

If then

$$\tan\psi=\frac{2r\sin\frac{\theta}{2}}{1-r^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

we have finally

$$\frac{A_1'}{A_1}=-\frac{(1+r^4-2r^2\cos\theta)^{\frac{1}{2}}}{1+r^2+2r\cos\frac{\theta}{2}}\,e^{-i\psi};$$

that is, the ray reflected from the first surface of the plate undergoes a phase-change of $(-\psi)$, the reduction factor or ratio of the *amplitude* of the reflected to that of the incident ray being

$$b=-\frac{(1+r^4-2r^2\cos\theta)^{\frac{1}{2}}}{1+r^2+2r\cos\frac{\theta}{2}}. \quad . \quad . \quad . \quad . \quad . \quad (13)$$

$b$ is a function of the period and damping of the wave-train as well as of the properties of the reflector. If the wave-train be not damped, we have

$$\left.\begin{aligned} \chi &= 90^\circ, \\ \rho &= \sqrt{1+\left(\frac{\alpha_2}{p_2\beta_2}\right)^2}, \\ \cos\theta &= \frac{1}{\rho}, \end{aligned}\right\} \quad . \quad . \quad . \quad (14)$$

so the expression for $b$ remains unaltered in form, $b$ being still a function of the period.

But if the conductivity of the electrolyte or $\alpha_2$ be zero, the angle $\theta$ becomes likewise zero, $\rho$ is unity, and we get the ordinary value for $b$, namely,

$$b=\frac{1-\sqrt{\frac{\beta_1}{\beta_2}}}{1+\sqrt{\frac{\beta_1}{\beta_2}}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

the period and damping of the incident ray having vanished from the expression.

The phase-change $\psi$ is zero for either a perfect insulator or a perfect conductor; $\theta$ becoming indefinitely small in the first case, and $r$ in the second.

The refracted wave is dealt with in exactly the same manner. Taking the value of $\frac{B_2}{A_1}$ from (8), and substituting in it the value of $\lambda$ from (11) we have

$$\frac{B_2}{A_1}=\frac{2\lambda}{\lambda+1}=\frac{2re^{\frac{i\theta}{2}}}{1+re^{\frac{i\theta}{2}}}$$

$$=\frac{2re^{\frac{i\theta}{2}}\left(1+r\cos\frac{\theta}{2}-ri\sin\frac{\theta}{2}\right)}{1+r^2+2r\cos\frac{\theta}{2}}.$$

If we write

$$\tan\psi'=\frac{r\sin\frac{\theta}{2}}{1+r\cos\frac{\theta}{2}}, \quad . \quad . \quad . \quad . \quad (16)$$

then
$$\frac{B_2}{A_1}=\frac{2r}{\sqrt{1+r^2+2r\cos\frac{\theta}{2}}}e^{i(\theta/2-\psi')}.$$

Thus for the transmitted ray at the dielectric-electrolyte surface, the change of phase is $\frac{\theta}{2}-\psi'$, and the ratio of its amplitude to that of the incident ray or $c$ is

$$c=\frac{2r}{\sqrt{1+r^2+2r\cos\frac{\theta}{2}}}. \quad . \quad . \quad . \quad . \quad (17)$$

$c$, like $b$, is a function of the period and damping of the incident ray ; like $b$ it remains a function of the period even for an undamped ray ; and like $b$ it becomes a function of the dielectric constants only, if the "electrolyte" be a perfect insulator, the expression in (17) becoming

$$c=\frac{2\sqrt{\frac{\beta_1}{\beta_2}}}{1+\sqrt{\frac{\beta_1}{\beta_2}}}. \quad . \quad . \quad . \quad . \quad . \quad (17a)$$

We have now sufficient data to determine the speed of propagation and wave-length in the electrolyte, before going on to deal with the reflexions and refractions at the second surface. Referring back to equation (4) for $X_2$, and substituting the values we have determined for $B_2$, $p$, and $q$, we have

$$X_2=cA_1e^{i(\theta/2-\psi')}e^{(-p_1+ip_2)t}e^{\eta\sqrt{\beta_2\rho}\{\cos(\chi+\theta/2)-i\sin(\chi+\theta/2)\}x},$$

or retaining only the real terms

$$X_2=cA_1e^{-p_1t+\eta\sqrt{\beta_2\rho}\cos\left(\chi+\frac{\theta}{2}\right)x}\cos\left\{p_2t-\eta\sqrt{\beta_2\rho}\sin\left(\chi+\frac{\theta}{2}\right)x\right.$$
$$\left.+\frac{\theta}{2}-\psi'\right\}. \quad . \quad . \quad . \quad (18)$$

Hence the speed of the wave in the electrolyte is

$$V_2=\frac{p_2}{\eta\sqrt{\beta_2\rho}\sin\left(\chi+\frac{\theta}{2}\right)}=\frac{\sin\chi}{\sqrt{\beta_2\rho}\sin\left(\chi+\frac{\theta}{2}\right)}, \quad . \quad (19)$$

and the wave-length

$$\lambda_2 = \frac{2\pi}{\eta\sqrt{\beta_2\rho}\sin\left(\chi+\frac{\theta}{2}\right)}. \quad . \quad . \quad . \quad (20)$$

But for the incident wave-train

$$\lambda_1 = \frac{2\pi}{p_2\sqrt{\beta_1}},$$

therefore

$$\frac{\lambda_2}{\lambda_1} = \sqrt{\frac{\beta_1}{\beta_2}}\frac{p_2}{\eta\sqrt{\rho}\sin\left(\chi+\frac{\theta}{2}\right)}$$

$$= \sqrt{\frac{\beta_1}{\beta_2}}\frac{\sin\chi}{\sqrt{\rho}\sin\left(\chi+\frac{\theta}{2}\right)} \quad . \quad . \quad . \quad . \quad (21)$$

$\rho$ and $\theta$ being both functions of $\alpha_2$ and of the period, and $\chi$ being a function of the rate of damping of the wave-train, $\frac{\lambda_2}{\lambda_1}$ is (like $b$ and $c$ and the phase-changes) a function of period, damping, and conductivity, except when the latter is zero: when we have simply

$$\frac{\lambda_2}{\lambda_1} = \sqrt{\frac{\beta_1}{\beta_2}}. \quad . \quad . \quad . \quad . \quad . \quad (21a)$$

### III. *The Phenomena at the Second Surface of the Plate.*

We now proceed to the inverse case where the wave is passing from the electrolyte into the dielectric.

If $X_2$ represent as before the electric force in the electrolyte, and $X_3$ represent the electric force in the second dielectric, we may now write

$$X_2 = B_1 e^{p(t-qz)} + B_1' e^{p(t+qz)}, \quad . \quad . \quad . \quad . \quad (22)$$

$$X_3 = A_3 e^{p(t-\sqrt{\beta_1}z)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

the wave in the electrolyte consisting of a direct and a reflected train, and that in the dielectric of a direct train only.

Applying the interface conditions as in the last section, we get for $z=0$

$$B_1 + B_1' = A_3, \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

$$\frac{dX_2}{dz} = \frac{dX_3}{dz}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

Carrying out the differentiation of (25) and putting $z=0$,

$$-p\sqrt{\beta_1}A_3=pq(-B_1+B_1'),$$

or

$$B_1-B_1'=A_3\frac{\sqrt{\beta_1}}{q}=A_3\lambda. \quad . \quad . \quad . \qquad (26)$$

Solving for $\frac{B_1'}{B_1}$ and $\frac{A_3}{B_1}$ from (24) and (26) we get

$$\left.\begin{aligned}\frac{A_3}{B_1}&=\frac{2}{1+\lambda}\\ \frac{B_1'}{B_1}&=\frac{1-\lambda}{1+\lambda}\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (27)$$

Using our previous notation of

$$\lambda=re^{\frac{i\theta}{2}}$$

and rationalizing, we obtain finally for the transmitted ray

$$\frac{A_3}{B_1}=\frac{2}{\sqrt{1+r^2+2r\cos\frac{\theta}{2}}}e^{-i\psi'},$$

so that the phase-change for the wave emerging from the electrolyte is $-\psi'$ (equation 16), and the reduction factor

$$f=\frac{2}{\sqrt{1+r^2+2r\cos\frac{\theta}{2}}}. \quad . \quad . \quad . \quad . \qquad (28)$$

The expression for $\frac{B_1'}{B_1}$ in (27) is the same as that for $\frac{A_1'}{A_1}$ in (8) except for the reversal of sign, so the phase-change at the second surface of the electrolyte is the same $(-\psi)$ in magnitude and sign as at the first surface, and the reduction factor

$$e=-b. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (29)$$

If the electrolyte be replaced by an insulator, $f$ takes the ordinary form

$$f=\frac{2}{1+\sqrt{\frac{\beta_1}{\beta_2}}}, \quad . \quad . \quad . \quad . \quad . \qquad (30)$$

and the relation

$$cf=1-b^2$$

holds. In the general case there is no such relation.

### IV. *The Intensity of the Transmitted Ray.*

We have now all the data necessary for treating the general case of a wave-train passing through a plate of finite thickness. We will first take the incident wave-train and follow its history in detail to obtain the expressions for the rays emergent after 0, 2, 4, . . . &c. internal reflexions. Let the incident wave-train be given by

$$\mathrm{A}\, e^{p(t-\sqrt{\beta_1}z)}$$

from the time $t=0$ onwards, $p$ being a complex quantity as defined by (9). Passing through the first surface and reaching the second the wave becomes ($d$ being the thickness of the electrolyte)

$$\mathrm{A}\, c\, e^{p(t-qd)}\, e^{i(\theta/2-\psi')},$$

and emerges in the form

$$\mathrm{A} cf\, e^{-pqd}\, e^{i(\theta/2-2\psi')}\, e^{p(t-\sqrt{\beta_1}z)}. \quad . \quad . \quad . \qquad \text{(I.)}$$

If we take the instant at which the incident wave first strikes the plate as the origin of time, the wave-train (I.) begins to emerge at time

$$t_2 = \frac{d \,.\, \eta \,.\, \sqrt{\beta_2 \rho} \,.\, \sin\left(\chi + \frac{\theta}{2}\right)}{p_2}, \quad . \quad . \quad . \qquad (31)$$

by equation (19).

The wave reflected from the second surface at the time that (I.) emerges is

$$-\mathrm{A} \,.\, bc\, e^{-pqd}\, e^{p(t+qz)}\, e^{i(\theta/2-\psi'-\psi)},$$

which becomes on reflexion at the first surface

$$\mathrm{A} \,.\, b^2 c\, e^{-2pqd}\, e^{p(t-qz)}\, e^{i(\theta/2-\psi'-\psi)},$$

and emerges from the second surface at time $3t_2$ as

$$\mathrm{A} b^2 cf e^{-3pqd} e^{p(t-\sqrt{\beta_1}z)} e^{i(\theta\ -2\psi'-2\psi)}. \quad . \quad . \quad . \quad . \qquad \text{(II.)}$$

This is the second emergent ray, or the ray emerging after two internal reflexions. The third emergent ray will be

$$\mathrm{A} b^4 cf e^{-5pqd}\, e^{i(\theta/2-2\psi'-4\psi)} e^{p(t-\sqrt{\beta_1}z)}, \quad . \quad . \quad . \qquad \text{(III.)}$$

emerging at time $5t_2$; and so on for the others. The $(n+1)$th emergent ray, or the ray emerging after $2n$ internal reflexions, is

$$Ab^{2n}cfe^{-(2n+1)pqd}e^{i(\theta/2-2\psi'-2n\psi)}e^{p(t-\sqrt{\beta_1}x)},$$

which emerges at time $(2n+1)t_2$. Remembering that

$$p=-p_1+p_2i=\eta(-\cos\chi+i\sin\chi),$$

$$q=\frac{\sqrt{\beta_1}}{\lambda}=\sqrt{\beta_2\rho}\left(\cos\frac{\theta}{2}-i\sin\frac{\theta}{2}\right),$$

this becomes

$$Acfb^{2n}e^{(2n+1)\kappa d}e^{-p_1t}e^{i[p_2t+\alpha-(2n+1)(p_2t_2+\psi)]}, \quad . \quad . \quad . \quad (32)$$

where we have written for brevity

$$\left.\begin{aligned}\eta\sqrt{\beta_2\rho}\cos\left(\frac{\theta}{2}+\chi\right)&=\kappa,\\ \frac{\theta}{2}-2\psi'+\psi&=\alpha.\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (33)$$

Finally, if we take the initial form of the wave-train to be given by the sine terms, we may write this ray emerging after $2n$ internal reflexions, $y_n$, as

$$y_n=A\,.\,cf\,.\,b^{2n}e^{(2n+1)\kappa d}e^{-p_1t}\sin\left[p_2t+\alpha-\overline{2n+1}(p_2t_2+\psi)\right]. \quad (34)$$

However small $\psi$ may be it should evidently be retained, as it may become of importance owing to the multiple reflexions.

The wave-train $y_n$ emerges at time $\overline{2n+1}t_2$. From $\overline{2n+1}t_2$ to $\overline{2n+3}\,t_2$, $y_0$ to $y_n$ inclusive are the only wave-trains in existence. The total energy of any wave-train varies as the time-integral of the square of the "displacement"

$$(y), \text{ or } (y_0+y_1+y_2+\ldots+y_n).$$

We will call this time-integral the *intensity* of the wave-train (or set of wave-trains forming the ray), though we are not using intensity in its ordinary sense.

To get the intensity of the ray transmitted through the plate, we shall then have to sum up a series of integrals partly of squares $(y_0^2, y_1^2, \ldots y_n^2)$ and partly of products $(2y_m\,y_n$ &c.) :

that is to say, if we call the intensity of the transmitted ray $I_t$,

$$I_t = \mathop{S}_{n=0}^{n=\infty} \int_{\overline{2n+1}t_2}^{\infty} y_n^2\, dt + 2 \mathop{S}_{m=0}^{m=n-1} \mathop{S}_{n=1}^{n=\infty} \int_{\overline{2n+1}t_2}^{\infty} y_m\, y_n\, dt. \quad . \quad . \quad (35)$$

In the experimental case the deflexions of the electrometer at E, fig. 1, are proportional to $I_t$.

We have now to get out the integrals in (35) and sum them. We will first multiply out the product $y_m y_n$ from the expression for $y_n$ given in (34). This can then be integrated, and the integral of $y_n^2$ obtained by putting $m=n$.

Writing, for brevity,

$$p_2 t_2 + \psi = \delta, \quad . \quad . \quad . \quad . \quad . \quad (36)$$

$$\begin{aligned} y_m\, y_n &= A^2 c^2 f^2\, b^{2(n+m)} e^{-2p_1 t} e^{2(m+n+1)\kappa d} \\ &\qquad \times \sin(p_2 t + \alpha - \overline{2n+1}\delta) \sin(p_2 t + \alpha - \overline{2m+1}\delta) \\ &= \tfrac{1}{2} A^2 c^2 f^2 b^{2(n+m)} e^{-2p_1 t} e^{2(m+n+1)\kappa d} \\ &\qquad \times \{\cos[2(m-n)\delta] - \cos 2[p_2 t + \alpha - (m+n+1)\delta]\}. \quad (37) \end{aligned}$$

Integrating,

$$\int_{\overline{2n+1}t_2}^{\infty} y_m\, y_n \,.\, dt = \tfrac{1}{2} A^2 c^2 f^2 b^{2(m+n)} e^{2(m+n+1)\kappa d}$$

$$\times \left[ \frac{-e^{-2p_1 t} \cos 2(m-n)\delta}{2p_1} + \frac{e^{-2p_1 t}}{2\eta} \cos\{2(p_2 t + \alpha) + \chi - 2(m+n+1)\delta\} \right]_{\overline{2n+1}t_2}^{\infty}.$$

The expression in the square brackets vanishes at the upper limit; so we have, substituting $\eta \cos\chi$ for $p_1$ in the denominator of the first fraction,

$$\int_{\overline{2n+1}t_2}^{\infty} y_m\, y_n \,.\, dt = \frac{1}{4\eta} A^2 c^2 f^2 b^{2(m+n)} e^{2(m+n+1)\kappa d}$$

$$\times e^{-2(2n+1)p_1 t_2} \left\{ \frac{\cos 2(m-n)\delta}{\cos\chi} - \cos[2(n-m)p_2 t_2 + 2\alpha + \chi \atop \qquad - 2(m+n+1)\psi] \right\}. \quad (38)$$

If we put $m=n$, we get

$$\int_{\overline{2n+1}t_2}^{\infty} y_n^2\, dt = \frac{1}{4\eta} A^2 c^2 f^2 b^{4n} e^{(4n+2)\kappa d} e^{-(4n+2)p_1 t_2}$$

$$\times \{\sec\chi - \cos[2\alpha + \chi - (4n+2)\psi]\}. \quad (39)$$

Having now got the integrals, we must next perform the summations indicated in (35). Let us take the $y_n^2$ integrals first: we have to sum the expression on the right-hand side of (39) from $n=0$ to $n=\infty$. The two terms in the bracket are best taken separately: the first forms a simple geometric series whose sum is

$$\frac{1}{4\eta}\mathrm{A}^2 . c^2 f^2 . \frac{e^{2(\kappa d-p_1t_2)}\sec\chi}{1-b^4e^{4(\kappa d-p_1t_2)}} . \quad . \quad . \quad . \quad . \qquad (40)$$

The second term requires different treatment, as the cosine is a function of $n$. We may take the cosine to be the real part of

$$e^{i(2\alpha+\chi-\overline{4n+2}\psi)},$$

and thus obtain again a geometrical series, the sum of which is

$$\frac{1}{4\eta}\mathrm{A}^2 . c^2 f^2 . \frac{e^{2(\kappa d-p_1t_2)} . e^{i(2\alpha+\chi-2\psi)}}{1-b^4e^{4(\kappa d-p_1t_2)}e^{-4i\psi}}.$$

This is rationalized by multiplying numerator and denominator by $1-b^4e^{4(\kappa d-p_1t_2)}e^{4i\psi}$; and to further abbreviate the expression we will write

$$\left.\begin{aligned} be^{\kappa d-2p_1t_2} &= \xi, \\ be^{\kappa d} &= \omega, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (41)$$

thus obtaining for the sum of the second terms of (39),

$$\frac{1}{4\eta}\mathrm{A}^2c^2f^2 . \frac{\omega\xi}{b^2} . e^{i(2\alpha+\chi-2\psi)}\frac{1-\omega^2\xi^2e^{4i\psi}}{1-2\omega^2\xi^2\cos 4\psi+\omega^4\xi^4}.$$

Remembering that

$$\alpha = \frac{\theta}{2}-2\psi'+\psi,$$

and writing

$$\theta-4\psi'+\chi = \phi, \quad . \quad . \quad . \quad . \qquad (42)$$

this becomes, retaining the real terms only,

$$\frac{1}{4\eta}\mathrm{A}^2c^2f^2 . \frac{\omega\xi}{b^2} . \frac{\cos\phi-\omega^2\xi^2\cos(\phi+4\psi)}{1-2\omega^2\xi^2\cos 4\psi+\omega^4\xi^4}. \quad . \qquad (43)$$

Adding (40) and (42) together, we get for $\mathrm{I}_1$, the portion of the transmitted intensity due to the square terms,

$$\mathrm{I}_1 = \mathrm{A}^2\frac{c^2f^2 . \omega\xi}{4\eta b^2}\left\{\frac{\sec\chi}{1-\omega^2\xi^2}-\frac{\cos\phi-\omega^2\xi^2\cos(\phi+4\psi)}{1-2\omega^2\xi^2\cos 4\psi+\omega^4\xi^4}\right\}. \qquad (44)$$

We have now to sum the product terms. We require

$$\mathrm{I}_2 = 2 \mathop{\mathrm{S}}_{n=1}^{n=\infty} \mathop{\mathrm{S}}_{m=0}^{m=n-1} \int_{\overline{2n+1}\,t_2}^{\infty} y_m y_n \, dt$$

$$= \mathrm{I}_2' - \mathrm{I}_2'',$$

say ; $\mathrm{I}_2'$ being the sum of the terms multiplied by $\sec\chi$, and $\mathrm{I}_2''$ the sum of the second terms. The integrated expression is given in (38). Taking the $\sec\chi$ terms first,

$$\mathrm{I}_2' = \frac{\mathrm{A}^2 . c^2 f^2}{2\eta b^2} \mathop{\mathrm{S}}_{n=1}^{n=\infty} \omega^{2n+2} e^{-(4n+2)p_1 t_2} \sec\chi \mathop{\mathrm{S}}_{m=0}^{m=n-1} \omega^{2m} \cos 2(m-n)\delta \, ;$$

$\cos 2(m-n)\delta$ may be treated as the real part of $e^{2i(m-n)\delta}$, or

$$\omega^{2m} \cos 2(m-n)\delta = e^{-2in\delta}(\omega^2 e^{2i\delta})^m,$$

which is a geometric series whose sum from 0 to $n-1$ is

$$e^{-2in\delta} \frac{1-(\omega^2 e^{2i\delta})^n}{1-\omega^2 e^{2i\delta}}.$$

Multiplying numerator and denominator by $1-\omega^2 e^{-2i\delta}$ to rationalize, and retaining only the real quantities in the numerator, this becomes

$$\frac{\cos 2n\delta - \omega^{2n} - \omega^2 \cos(2n+2)\delta + \omega^{2n+2}\cos 2\delta}{1-2\omega^2\cos 2\delta + \omega^4}.$$

Therefore

$$\mathrm{I}_2' = \frac{\mathrm{A}^2 . c^2 f^2}{2\eta b^2} \frac{\sec\chi}{1-2\omega^2\cos 2\delta+\omega^4} \mathop{\mathrm{S}}_{n=1}^{n=\infty} (\cos 2n\delta - \omega^{2n}$$
$$- \omega^2 \cos(2n+2)\delta + \omega^{2n+2}\cos 2\delta)\,\omega^{2n+2} e^{-(4n+2)p_1 t_2}.$$

The first and third terms in the bracket may be summed together, as also the second and fourth. Carrying out the summation as before, we get

$$\mathrm{I}_2' = \frac{\mathrm{A}^2 c^2 f^2}{2\eta b^2} \frac{\sec\chi . \omega\xi}{1-2\omega^2\cos 2\delta+\omega^4} \left\{ \frac{\xi^2(\cos 2\delta - \xi^2) - \omega^2\xi^2(\cos 4\delta - \xi^2\cos 2\delta)}{1-2\xi^2\cos 2\delta+\xi^4} \right.$$
$$\left. -(1-\omega^2\cos 2\delta)\frac{\omega^2\xi^2}{1-\omega^2\xi^2} \right\}.$$

Bringing the two fractions to a common denominator, $(1-2\omega^2\cos 2\delta+\omega^4)$ divides out, and

$$\mathrm{I}_2' = \frac{\mathrm{A}^2 c^2 f^2}{2\eta b^2} \frac{\sec\chi . \omega\xi}{1-\omega^2\xi^2} \frac{\xi^2(\cos 2\delta - \xi^2)}{1-2\xi^2\cos 2\delta+\xi^4} \quad . \quad . \quad . \quad (45)$$

# PROCEEDINGS

AT THE

# MEETINGS OF THE PHYSICAL SOCIETY

# OF LONDON.

## SESSION 1894-95.

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February 9th, 1894.

Prof. A. W. **Rücker**, President, in the Chair.

A paper was read by Mr. **Owen Glynne Jones**, B.Sc., on "The Viscosity of Liquids."

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February 23rd, 1894.

Prof. A. W. **Rücker**, President, in the Chair.

Mr. J. W. **Kearton** was elected a Member of the Society.

A note on "A New Electrical Theorem" was read by Mr. T. H. **Blakesley**.

Prof. C. V. **Boys**, F.R.S., read a note on "The Attachment of Quartz Fibres."

Mr. **Littlewood** read a note on "A Method of Determining Refractive Indices."

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March 9th, 1894.

Prof. A. W. **Rücker**, President, in the Chair.

Prof. O. **Henrici**, F.R.S., made a communication on "Mathematical Calculating Machines, especially a New Harmonic Analyser."

Mr. H. **Wilde**, F.R.S., exhibited and described his "Magnetarium."

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April 13th, 1894.

Prof. A. W. **Rücker**, President, in the Chair.

Mr. W. G. **Rhodes** was elected a Member of the Society.

A discussion upon Prof. **Henrici's** paper given at the last Meeting took place, and Mr. A. **Sharp**, B.Sc., read a paper on "An Harmonic Analyser."

Mr. P. L. **Gray**, B.Sc., read a paper on "The Minimum Temperature of Visibility."

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April 27th, 1894.

Prof. A. W. **Rücker**, President, in the Chair.

Dr. C. V. **Burton** read a paper "On the Mechanism of Electrical Conduction."

A paper by Prof. S. P. **Thompson**, F.R.S., and Mr. **Miles Walker**, "On the Design and Winding of Alternate-Current Electromagnets," was read.

Major R. L. **Hippesley**, R.E., read a paper on "A Graphical Method of Constructing the Curves of Current in Electromagnets and Transformers."

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May 11th, 1894.

Mr. **Walter Baily**, Vice-President, in the Chair.

A communication "On Electromagnetic Induction in Plane, Cylindrical, and Spherical Current Sheets, and its Representation by Moving Trails of Images" was made by G. H. **Bryan**, M.A.

A paper "On Dielectrics" was read by Mr. **Rollo Appleyard**.

Prof. **Minchin** made a communication "On the Behaviour of certain Bodies in presence of Electromagnetic Oscillations."

May 25th, 1894.

Prof. A. W. **Rücker**, President, in the Chair.

Prof. W. **Ramsay**, F.R.S., read a paper "On the Passage of Hydrogen through a Palladium Septum."

Prof. W. **Ramsay**, F.R.S., and Mr. E. C. C. **Baly** communicated a paper "On the Expansion of Rarefied Gases."

June 8th, 1894.

Prof. A. W. **Rücker**, President, in the Chair.

A discussion took place upon the paper by Prof. **Ramsay** and Mr. E. C. C. **Baly**, read at the last Meeting.

A paper "On the Isothermals of Ether," by Mr. **Rose Innes**, was read.

June 22nd, 1894.

Prof. W. E. **Ayrton**, Past President, in the Chair.

Captain **Abney**, F.R.S., exhibited Photographs of Flames.

Prof. O. **Henrici**, F.R.S., read a paper "On an Elementary Theory of Planimeters."

Mr. F. W. **Hill** made a communication "On the Hatchet Planimeter."

Mr. A. **Sharp**, B.Sc., made a communication on "A new Integrating Apparatus."

Prof. **Perry**, F.R.S., made a communication on "Magnetic Shielding."

Mr. S. **Skinner** made a communication "On Clark's Cells."

### October 26th, 1894.

Prof. A. W. RÜCKER, President, in the Chair.

A paper was read, "On the Influence of Temperature on the Specific Heat of Aniline," by E. H. GRIFFITHS, M.A.

### November 9th, 1894.

Prof. A. W. RÜCKER, President, in the Chair.

Messrs. D. RINTOUL, R. APPLEYARD, and W. BARLOW were elected Members of the Society.

A paper by Dr. J. LARMOR on "The Significance of Wiener's Localization of the Photographic Action of Stationary Light-Waves" was read by Mr. ELDER.

Dr. SYDNEY YOUNG, F.R.S., read a paper on "The Influence of the Relative Volumes of Liquid and Vapour on the Vapour-pressure of a Liquid at Constant Temperature."

Mr. BURKE read a paper, "On a Suggestion by Prof. J. J. Thomson in connexion with the Luminescence of Glass due to Kathode Rays."

### November 23rd, 1894.

Prof. A. W. RÜCKER, President, in the Chair.

Mr. J. BURKE was elected a Member of the Society.

Mr. WOMACK read a paper on "A Modification of the Ballistic Galvanometer Method of Determining the Electromagnetic Capacity of a Condenser."

Prof. S. P. THOMPSON, F.R.S., and Mr. MILES WALKER communicated a paper on "Mirrors of Magnetism."

Prof. W. E. AYRTON, F.R.S., and Mr. MATHER exhibited a "Student's Apparatus for Verifying Ohm's Law."

Prof. AYRTON also showed an Idiostatic Electrometer.

December 14th, 1894.

Prof. A. W. Rücker, President, in the Chair.

Messrs. G. H. Bryan, J. W. Capstick, T. C. Fitzpatrick, G. F. C. Searle, S. Skinner, W. C. D. Whetham, L. R. Wilberforce, and Major P. MacMahon, R.A., were elected Members of the Society.

Prof. W. E. Ayrton, F.R.S., and Mr. H. C. Haycraft communicated a paper on "Students' Simple Apparatus for Determining the Mechanical Equivalent of Heat."

Prof. W. E. Ayrton and Mr. E. A. Medley communicated a paper on "Tests of Glow-Lamps, and Description of the Measuring Instruments employed."

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January 11th, 1895.

(Held by invitation of Professor Carey Foster at the Physical Laboratory of University College.)

Prof. A. W. Rücker, President, in the Chair.

Prof. Ramsay and Miss Dorothy Marshall communicated a paper on "The Measurement of Latent Heats of Vaporization of certain Organic Liquids."

Mr. Eumorfopoulos read a paper on "The Determination of Thermal Conductivity and Emissivity."

Mr. A. W. Porter read a paper on "The Influence of the Dimensions of a Body upon the Thermal Emission from its Surface."

Mr. G. U. Yule communicated a paper on "The Passage of an Oscillator Wave-train through a Plate of Conducting Dielectric."

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January 25th, 1895.

Prof. A. W. Rücker, President, in the Chair.

Prof. W. T. A. Emtage was elected a Member of the Society.

Prof. W. E. Ayrton, F.R.S., and Mr. Medley continued the paper (begun Dec. 14th, 1894) on "Tests of Glow-Lamps, and Description of the Measuring Instruments employed."

Prof. Anderson and Mr. J. A. McClelland communicated a paper on "The Temperature of Water at its Maximum Density, and its Coefficient of Expansion in the Neighbourhood of this Temperature."

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## *Annual General Meeting.*

February 8th, 1895.

Prof. A. W. Rücker, President, in the Chair.

The following Report of the Council was read by the Chairman:—

Within the year which has elapsed since the last Annual General Meeting very considerable changes have been carried out in the directions indicated in the last Report. The Council has set on foot the monthly issue of a publication which contains Abstracts of important Foreign papers as well as papers which have been submitted directly to the Society.

A valuable list of the chief Memoirs on Physics of Matter, compiled by Mr. R. A. Lehfeldt, has been published by the Society, and a copy of this pamphlet has been sent to every Member.

The place of Meeting has been changed, and it is hoped that, on the whole, Members will find these rooms, in which, by the kind arrangement of the Chemical Society, we are now enabled to meet, rather more convenient and accessible than our old home at South Kensington. In saying this, however, the Council wishes emphatically to express the sense of its Members of the great advantages which, during the youth of this Society, have accrued to it from the kind way in which the rooms at S. Kensington have been placed at its service by the Lords' Committee of the Council on Education.

Tea and coffee are now provided before the Meetings.

Since the last General Meeting there have been fifteen Ordinary Business Meetings. Thirteen of them have been held at the usual place, one under special circumstances at the Institute of the City and Guilds of London, with the permission of Prof. Ayrton, and one at the invitation of Prof. Carey Foster and the Staff of University College, Gower Street, at the newly organized Laboratory of that Institution.

The Members of the Society number now about 370.

A vacancy in the list of Honorary Members has taken place in the death of Herr H. von Helmholtz.

The other deaths in the ranks of the Society, news of which has reached the Council, are those of Mr. A. C. Ranyard, Col. Armstrong, and Mr. Alder Wright.

The following additions have been made to the Library during the past year:—

*Newspapers and Magazines*:—

Nature.
The Electrical Review.
The Electrician.
Electrical Plant.
Engineering.
Industries and Iron.
The Open Court.
The Philosophical Magazine.
Journal de Physique.
Beiblätter.
Annalen der Physique und Chemie.

*Journals of Societies, British*:—

Journal of the Society of Arts.
Proceedings of the Birmingham Philosophical Society.
Transactions and Proceedings of the Cambridge Philosophical Society.
Journal of the Camera Club.
Transactions and Proceedings of the Royal Dublin Society.
Journal of the Institute of Electrical Engineers.
Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Proceedings of the Institute of Mechanical Engineers.
Quarterly Journal of the Royal Meteorological Society.
Proceedings of the Royal Institution.
Proceedings of the Royal Society.

*Journals of Societies, Colonial*:—

Journal and Proceedings of the Royal Society of New South Wales.
Geological and Natural History Survey of Canada.
Hong Kong Observatory Observations.
Proceedings and Transactions of the Nova Scotia Institute of Natural Science.
Transactions of the Canadian Institute.
Papers of the Mathematical and Physical Society of Toronto.

*Journals of Societies, Foreign*:—

Proceedings of the Academy of Natural Sciences, Philadelphia.
Journal of the Physical and Chemical Society of Russia.
Verhandlungen, Berlin Physical Society.
Mémoires and Séances of the Physical Society of France.
Journal of the College of Science of Japan.
Séances and Bulletin International de l'Académie des Sciences, Cracovie.
Report of the Ohio Meteorological Bureau.
Technology Quarterly and Proceedings of the Society of Arts, Massachusetts.
Report of the Ohio Weather and Crop Service.
Prace Matematyczno-Fizyczne, Warsaw.

*Books, &c.*:—

Norwegian North Sea Expedition, xxii.
Bureau International des Poids et Mesures. Travaux et Mémoires, viii.-x:
——. Seizième rapport.
On the Origin of Moss Gold, &c., by A. Liversidge.
Stonyhurst College Observatory Meteorological and Magnetical Observations.
Bombay Magnetical and Meteorological Observations.
Smithsonian Report.
Œuvres de Laplace, Tome x.
Catalogue of Books, Radcliffe Library, Oxford.
A New Story of the Stars, by A. W. Bickerston.
Kew Observatory Report.
The Electric Current, by R. M. Walmsley.
Calendars of University College and Imperial University of Japan.

**Hermann Ludwig Ferdinand von Helmholtz**, Honorary Member of the Society, was born August 31, 1821, at Potsdam, where his father, Ferdinand Helmholtz, was Professor in the Gymnasium. His mother, Caroline Penn, was of an English family which had emigrated to Prussia. In early years he was delicate, as he tells us in the autobiographical address delivered on the occasion of his seventieth birthday in 1891. His first scientific ideas came to him when a child playing with his wooden blocks. His father used to take him about much in the neighbourhood of Potsdam, and encouraged in him the love of Nature. Hence, he says, his first fragments of Physics had more interest for him than purely geometrical and algebraical studies. He was fascinated by the intellectual mastery over nature given by the logical force of law.

The books on Physics he could read in his father's library were old. "Phlogiston held sway; galvanism had not grown beyond the voltaic pile;" spectacle-glasses afforded a means of experiments with lenses; and the theory of the telescope had more of interest for him than Cicero or Virgil.

But Physics offered no means of livelihood to its student; and so he entered the Army Medical School at Berlin, becoming a pupil of Johannes Müller. In early days he began to consider the nature of Vital Force; the ideas then in favour among physiologists were those of Stahl, and Helmholtz, reflecting on them, was led to see that Stahl's theory "ascribed to every living body the nature of a *perpetuum mobile*." From this grew the Essay "On the Conservation of Force," published in 1847. The questions he placed before himself for solution were two: "What relations must exist between various kinds of natural forces for a perpetual motion to be possible?" and further, "Do these relations exist?" Most of the leading Physicists of his time were disposed to consider the essay a fantastical speculation. Jacobi alone of the older generation seems to have recognized its importance; the younger men received it with enthusiasm.

In 1848 Helmholtz became Assistant in the Anatomical Museum at Berlin, and in the following year Professor of Physiology at Königsberg. In 1856 he was called to Bonn as Professor of Physiology and Anatomy, and in 1859 to Heidelberg as Professor of Physiology; in 1871 he was promoted to Berlin as Professor of Natural Philosophy. About 1887 the wise munificence of Werner von Siemens founded the Berlin Reichsanstalt, and Helmholtz became its first President. It was at Königsberg that he invented the ophthalmoscope, and "had the joy of being the first to see clearly before him a living human retina." From this time success was assured. His colleagues and the authorities recognized his genius, and for the future he was able to pursue far more freely "the secret impulses of his desire for knowledge."

The work on Physiological Optics followed. Helmholtz had the thorough grasp of Physical principles needed for success in the task which he undertook. A full analysis of the book is far beyond our limits; it deals first with the laws of refraction at spherical surfaces: the theory of colour sensation is then investigated, and its dependence on three variables, in accordance with the ideas of Young, is proved conclusively. Another difficult subject which is carefully treated is that of the motions of the eyes. The question whether there are three primary sensations in the eye corresponding to the three variables of the colour equations remains unsolved. Maxwell's experiments and Helmholtz' work have proved the existence of these three variables, and have shown that any theory which is to explain colour vision must take account of them.

In 1862 was published the first edition of the 'Sensations of Tone as a Physiological Basis for the Theory of Music.' In it the laws of Acoustics are considered from a Physical as well as from a Physiological standpoint, and the relation between the two is shown. The methods of analysing a compound tone into its simple notes are due to him: the work is full of brilliant suggestions and carefully elaborated results.

By this time the Physiologist had become a Physicist and the Physicist a Mathematician. The call to Berlin left him free to develop the ideas which had first shown themselves in the Essay in 1847; and though his interest in Physiology never waned, and in some respects grew stronger, his own work from this time onwards was Physical.

It is impossible to describe here in any detail what that work was. He has written on nearly every branch of our science, and each subject that he has handled has gained from his powerful treatment. "I have been in a position," he writes, "to solve several mathematical physical problems. . . . But the pride which I might have felt about the final result in these cases was considerably lowered by my consciousness that I had only succeeded in solving these problems after many devious ways by the gradually increasing generalization of favourable examples and by a series of fortunate guesses. . . . I had to compare myself with an Alpine climber who, not knowing his way, ascends slowly and with toil, and is often compelled to retrace his steps because his progress is stopped; sometimes by reasoning, sometimes by accident, he hits upon traces of a fresh path, which again leads him a little further, till at last the summit is reached."

We think of Newton, who describes himself as seeking stones upon a shore, and occasionally finding a pebble more precious than any discovered by the crowd about him; but surely rather, compared with those who struggle to follow where he has led, von Helmholtz was no ordinary Alpine climber, but the Prince of Alpine guides, who, after surveying from a distance an unknown peak, and carefully maturing his plan, leads his party to the top with an unerring skill which is little short of marvellous. He has helped us, however, in our struggles onwards by his assurance that his brilliant suggestions did not come without effort on his part.

"Such moments of fruitful thought," he writes, "were indeed very delightful; but not so the reverse when the redeeming ideas did not come. For weeks or months I was gnawing at such a question until in my mind I was

'Like to a beast upon a barren heath,
Dragged in a circle by an evil spirit,
While all around are pleasant pastures green.'

And lastly, it was often a sharp attack of headache which released me from this strain, and set me free for other interests."

The Physical papers really began in 1847 with the Essay "On the Conservation of Force"—one could wish the translator had said Energy—and were continued to within a short time of his death last year.

His collected papers were issued in two volumes in 1882 and 1883, each containing about 1000 pages. Of these the first volume and some 200 pages of the second contain physical and mathematical writings.

In his paper "On Vortex Motion" (1858) he—to use Maxwell's words—"establishes principles in pure hydrodynamics which had escaped the penetrative powers of all the mathematicians who preceded him, including Lagrange himself."

The Acoustical papers we have already referred to. Of his Optical work, in addition to the Physiological Optics, the paper on Anomalous Dispersion, published in 1874, is perhaps the most important.

Among the theoretical Electrical papers must be mentioned one on Electrical Oscillations, published in 1869, containing some of the first measurements on the period of an oscillatory discharge of a condenser through a circuit having self-induction. The most important of Helmholtz' contributions to Electrical theory, however, are contained in his papers on the Theory of Electrodynamic Action. The first of these, dealing with the Equations of Motion of Electricity in Conductors at rest, appeared in Borchardt's Journal, vol. lxxii., in 1870; others followed in 1871 and 1873. A short paper on the Laws of Variable Electric Currents in Solid Conductors, giving a general summary of the results of the full paper in Borchardt's Journal, was read at the meeting of the Naturhistorich-medicinischer Verein at Heidelberg in 1870. Maxwell's great paper on the general equations of the electromagnetic field was published in the 'Philosophical Transactions' for 1865.

In the paper in Borchardt's Journal, Helmholtz obtains equations more general in form than those of Maxwell. He starts by finding the complete expression for the mutual potential energy of two elements of current consistent with Ampère's laws for closed circuits. This expression involves an unknown constant $k$; the terms containing $k$ disappear whenever the circuits are completely closed; hence the existence of this quantity cannot be proved from experiments on closed circuits. According to Maxwell's theory $k$ is zero; and in this case the only electromagnetic waves which can be propagated are transverse waves. According to Helmholtz' more general form, electrostatic potential is propagated through a dielectric by longitudinal waves which travel with velocity $V/\sqrt{k}$, where V is the velocity of the transverse disturbance. J. J. Thomson's Report on Electrical Theories (Brit. Assoc. Reports, Aberdeen, 1885) gives an account of the efforts made up to that time to determine $k$ and to decide between the two theories, but without success, until in 1888 Helmholtz' most brilliant pupil, Hertz *, astonished the world by his complete verification of Maxwell's theory.

Less than two years ago von Helmholtz contributed his last notable paper to Electromagnetic theory, dealing with Dispersion.

Space compels only the very briefest reference to his work on

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* Hertz' own original results did not, it is true, confirm Maxwell's theory completely; the further experiments of Sarasin and de la Rive were needed before all errors were eliminated and the proof made perfect.

Thermodynamics and Chemistry, specially in reference to the actions which take place in a battery, the connexion between its electromotive force and the chemical combinations which occur together with what one may call his electrical theory of chemical action.

Specially interesting, however, to many Members of the Physical Society is his work in connexion with Electrical Units. In his official position as Head of the Reichsanstalt it fell to him to frame the fundamental definitions of the units, and to draft the laws by which those units were legalized in Germany. His visit to England in 1892 was undertaken with a view to securing uniformity in the fundamental definitions throughout the world; and the successful results of the Conference at Edinburgh in that year and the Congress at Chicago in 1893 are in no small measure due to him. Those of us who were then brought into close contact with him were amazed at his marvellous grasp of the small details involved in the various experiments, no less than at the width and clearness of his knowledge.

It is impossible to express in words the debt which Physicists owe to von Helmholtz: his works and the gratitude of his pupils on every hand form his best memorial. The words of the great wise man of old times have already been applied to him; it is fitting that they should again be quoted here—

> "A wise man instructeth his people, and the fruits of his understanding fail not."
>
> "A wise man shall inherit glory among his people, and his name shall be perpetual."

Col. **Robert Young Armstrong** was of Irish descent, and entered the Royal Engineers in 1858. After serving abroad he returned to England, and was quartered at Chatham, where he was appointed first, Assistant Instructor, and, secondly, Instructor in Electrical Science and Sub-marine Mining, which was then in its infancy. The Service is indebted to many improvements and inventions in this latter branch of defence, and his services were recognized by the Commander-in-Chief by his appointment as Inspector of Submarine Defences, and on his retirement from the Service by his being created a C.B. Col. Armstrong was elected to the Royal Society in 1891. His kindly disposition and unselfishness made him a general favourite with all, and there is no one whose loss could be more deplored by his friends, amongst whom the writer of this notice was proud to be reckoned.

**Arthur Cowper Ranyard** was born at Swanscombe, in the county of Kent, on June 21, 1845, and, after his father's removal to 13 Hunter Street, Brunswick Square, he was educated at University College School, Gower Street. On leaving the school he entered the adjoining college, where, from the influence of the late Professor De Morgan, whose classes he attended, he acquired a strong love for mathematics and astronomy. Whilst at University College he collaborated with Mr. George De Morgan in founding a "Students' Mathematical Society," which had a most successful career, developing eventually into the present "London Mathematical Society." Mr. Ranyard read the first paper before the new Society, one "On Determinants."

From University College, London, Mr. Ranyard went to Cambridge, entering on residence at Pembroke College in the October term of 1865, and taking his degree in 1868. Three years later he was called to the Bar at Lincoln's Inn; but, whilst adopting the law as his profession, his leisure hours were mostly devoted to science. Thus he joined the Physical Society in its first session, and in 1872 worked with Lord Lindsay (the present Earl of Crawford) in the study of photographic irradiation. Again in 1885 and 1886 the same subject of photography occupied his attention, and he conducted a number of experiments in order to determine the relations between the length of exposure and the intensity of photographic action.

His chief work as an astronomical observer consisted in his observations of the three total solar eclipses of 1872, 1878, and 1882. On the first occasion he was one of the observers sent out by the Joint Committee of the Royal and Royal Astronomical Societies, and was stationed at Villasmunda, near Augusta, Sicily. He was here favoured with much better fortune than awaited most of his colleagues, and was afforded a fine view of the phenomena of totality. The observations assigned to him were polariscopic, and he carried them out with entire success, repeating, with a few additional details, those made by Prazmowski in 1860. His expeditions to America to view the total solar eclipse of 1878, and to Egypt to view that of 1882, were made at his own expense, and he went on his own responsibility. He was contemplating an important work in the department of solar physics on the lines opened up by M. Deslandres and Professor Hale, when the disease which afterwards proved fatal laid its hand upon him. He had had a spectroheliograph constructed for him, and this he lent to Professor

Hale for the latter's expedition to Etna to attempt the photographing of the corona in full sunshine. Mr. Ranyard never had the opportunity of using the instrument himself, and it lay in its cases, not yet unpacked, at the time of his death.

Mr. R. A. Proctor's sudden death in 1887 left the publication of his great work, 'Old and New Astronomy,' in a most unfinished state, and his magazine, 'Knowledge,' without an editor. It was exceedingly typical of Mr. Ranyard's generous spirit that he cheerfully undertook the immense amount of hard work, extending over many months, which the completion of the 'Old and New Astronomy' involved, in order to sustain the reputation of his deceased friend and to assist his family. And difficult as it was to follow a man of Proctor's ability, and to sustain his work upon an equal level, Mr. Ranyard fully succeeded in the task.

Another publication undertaken by Mr. Ranyard was that of Professor De Morgan's little brochure, 'Sir Isaac Newton, his Friend, and his Niece,' to which he supplied a preface. Nor was the reputation of Sir Isaac Newton the only one in which he was interested. He was anxious that the gifted young pioneer of English astronomy should have due honour rendered to him, and was instrumental in having a memorial tablet erected to Jeremiah Horrox in Westminster Abbey.

His connexion with the Royal Astronomical Society began at an unusually early age, he having been elected a Fellow when only 18. His first work in an official capacity was in the preparation and organization of the Eclipse Expedition of 1870; Mr. J. Norman Lockyer being appointed Secretary of the Joint Eclipse Committee of the Royal and Royal Astronomical Societies, and Mr. Ranyard, Assistant-Secretary. He was elected to a seat on the Council in February 1872, and to the Secretaryship in February 1874. This office, which he retained till 1880, he filled with conspicuous industry and courtesy. During his tenure of this office he brought out vol. xli. of the 'Memoirs,' the great "Eclipse" volume. In its inception it was intended to be a report of the eclipses of 1860 and 1870, and at first Mr. Ranyard worked with the assistance and under the oversight of Sir G. B. Airy, then Astronomer Royal. Soon, however, the entire work devolved upon him, and its scope was extended until it embraced the collation and arrangement of the known observations of all eclipses down to 1878. This work, most admirably designed, and most laborious in execution, was not published until 1879.

Early in the summer of 1894 a mysterious loss of weight and other disquieting symptoms began to make themselves apparent. These were eventually traced to the formation of an internal cancer which all but precluded the possibility of nourishment entering the system. After a long and most trying illness, borne with great patience and hopefulness, he died on December 14, 1894, whilst the meeting of the Royal Astronomical Society, in the welfare of which he took from first to last so keen an interest, was in session. Mr. Ranyard was not married, and none of his immediate relatives survived him. But his purity of motive, his generous spirit, his freedom from self-seeking, and his unfailing courtesy of manner, endeared him to a large circle of friends who will keenly feel his loss. Amongst these will be numbered not a few of the most distinguished foreign astronomers, Mr. Ranyard having been an excellent linguist, and frequently visiting the Continent.

These details of Mr. Ranyard's career have been kindly furnished by the Royal Astronomical Society.

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The adoption of the Report was proposed and passed unanimously.

The election of Officers and other Members of Council then took place, the new Council being constituted as follows :—

*President.*—Capt. W. DE W. ABNEY, R.E., C.B., D.C.L., F.R.S.

*Vice-Presidents who have filled the Office of President.*—Dr. J. H. GLADSTONE, F.R.S. ; Prof. G. C. FOSTER, F.R.S. ; Prof. W. G. ADAMS, M.A., F.R.S. ; Lord KELVIN, D.C.L., LL.D., P.R.S. ; Prof. R. B. CLIFTON, M.A., F.R.S. ; Prof. A. W. REINOLD, M.A., F.R.S. ; Prof. W. E. AYRTON, F.R.S. ; Prof. G. F. FITZGERALD, M.A., F.R.S. ; Prof. A. W. RÜCKER, M.A., F.R.S.

*Vice-Presidents.*—WALTER BAILY, M.A. ; Major-General E. R. FESTING, R.E., F.R.S. ; Prof. J. PERRY, D.Sc., F.R.S. ; G. JOHNSTONE STONEY, M.A., F.R.S.

*Secretaries.*—T. H. BLAKESLEY., M.A., M.Inst.C.E. ; H. M. ELDER, M.A.

*Treasurer.*—Dr. E. ATKINSON.

*Demonstrator and Librarian.*—C. VERNON BOYS, F.R.S.

*Other Members of Council.*—SHELFORD BIDWELL, M.A., LL.B., F.R.S.; Prof. W. CROOKES, F.R.S.; L. FLETCHER, M.A., F.R.S.; R. T. GLAZEBROOK, M.A., F.R.S., G. GRIFFITH, M.A.; Prof. O. HENRICI, Ph.D., F.R.S.; Prof. G. M. MINCHIN, M.A.; J. SWINBURNE; Prof. S. P. THOMPSON, D.Sc., F.R.S.; Prof. S. YOUNG, D.Sc., F.R.S.

Votes of thanks were passed to the Lords' Committee of the Council on Education; to the OFFICERS; and to the AUDITORS.

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The following Resolution, of which notice had been duly given, was moved from the Chair and carried:—

"That the Articles of Association of the Society be altered in the manner following:—

> "(*a*) In Article 11, after the word 'member' to insert the words 'except as hereinafter appointed.'
>
> "(*b*) After Article 12, to insert 'Article 12 *a*. The Council may at their discretion recommend to the Society for election as a member any person not qualified according to Article 11, when in the opinion of at least three fourths of those present at the Council Meeting circumstances render it desirable to do so.'"

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## The Treasurer in Account with the Physical Society, from January 1st, 1894, to December 31st, 1894.

| *Dr.* | £ *s.* *d.* | £ *s.* *d.* |
|---|---|---|
| Balance in the Bank, January 1, 1894 | | 239 9 11 |
| Dividends, less Income Tax:— | | |
| £400 Furness 4 per cent. Debenture Stock | 15 10 4 | |
| £200 Lancaster Corporation Stock (3 half-years) | 11 13 0 | |
| £1900 Midland 4 per cent. Preference Stock | 38 15 10 | |
| £254$\frac{2}{9}$ New South Wales 3½ per cent. Stock | 8 12 4 | |
| £200 Metropolitan Board of Works Stock | 6 15 8 | |
| | | 81 7 2 |
| Taylor and Francis:— | | |
| Sales, less Commission | | 22 4 11 |
| Entrance-Fees | 10 0 0 | |
| Life Compositions | 90 0 0 | |
| Subscriptions for 1888 | 1 0 0 | |
| „ 1889 | 1 0 0 | |
| „ 1890 | 1 0 0 | |
| „ 1891 | 2 0 0 | |
| „ 1892 | 4 0 0 | |
| „ 1893 | 8 0 0 | |
| „ 1894 | 109 0 0 | |
| „ 1895 | 3 0 0 | |
| | | 229 0 0 |
| Balance due to the Treasurer | | 4 18 6 |
| | | £577 0 6 |

| *Cr.* | £ *s.* *d.* | £ *s.* *d.* |
|---|---|---|
| Jan. 1, 1894. Balance due to the Treasurer | | 2 18 0 |
| Taylor and Francis:— | | |
| Proceedings, vol. xii. (parts 3 and 4), and vol. xiii. (part 1) | 138 14 6 | |
| Members' separate copies | 22 14 6 | |
| Miscellaneous printing | 40 5 10 | |
| Postage and sending out | 13 17 6 | |
| Lehfeldt's Bibliography | 24 18 1 | |
| | | 240 10 5 |
| Williams and Norgate | | 6 4 4 |
| Chapman; Attendance and petty cash | | 5 14 1 |
| Reporting:— | | |
| Dr. Mather | 17 12 11 | |
| Dr. Burton | 4 14 6 | |
| | | 22 7 5 |
| Binding:— | | |
| Mr. Hovey | 3 7 1 | |
| Mr. Gyde | 1 19 3 | |
| | | 5 6 4 |
| Chemical Society:— | | |
| Hire of Rooms | | 6 16 6 |
| Lancaster Corporation Stock purchased | | 3 6 8 |
| Expenses of Tea | | 5 0 0 |
| Petty Cash:— | | |
| Dr. Atkinson | 1 8 0 | |
| Mr. Elder | 3 11 0 | |
| Mr. Blakesley (2 years) | 1 12 11 | |
| | | 6 11 11 |
| Balance in the Bank, Dec. 31, 1894 | | 272 4 10 |
| | | £577 0 6 |

EDMUND ATKINSON, *Treasurer.*

Examined and found to agree with the vouchers, books, and accounts.

RICHARD INWARDS, } *Auditors.*
A. P. TROTTER,

## PROPERTY ACCOUNT OF THE PHYSICAL SOCIETY, December 31, 1894.

| Assets. | £ | s. | d. | Liabilities. | £ | s. | d. |
|---|---|---|---|---|---|---|---|
| Balance at Bank | 272 | 4 | 10 | Subscriptions for 1895 in advance | 3 | 0 | 0 |
| Subscriptions due, estimated | 34 | 0 | 0 | Balance due to the Treasurer | 4 | 18 | 6 |
| £400 Furness 4 per cent. Debenture Stock | 456 | 0 | 0 | | | | |
| £1000 Midland 4 per cent. Preference Stock | 1194 | 0 | 0 | | | | |
| £200 Metropolitan Board of Works $3\frac{1}{2}$ per cent. Stock | 217 | 0 | 0 | | | | |
| £270 Lancaster Corporation 3 per cent. Stock | 227 | 6 | 8 | | | | |
| £254$\frac{2}{5}$ New South Wales $3\frac{1}{2}$ per cent. Inscribed Stock | 249 | 7 | 5 | Balance | 2642 | 0 | 5 |
| | £2649 | 18 | 11 | | £2649 | 18 | 11 |

EDMUND ATKINSON, *Treasurer*.

Securities examined and found correct. For the New South Wales $3\frac{1}{2}$ per cent. Stock no certificate is given. The Bankers have duly received the last dividend for October 1894.

RICHARD INWARDS, } *Auditors*.
A. P. TROTTER, }

Returning now to the second half of $I_2$, the term not containing sec $\chi$, we have

$$I_2'' = \frac{A^2 . c^2 f^2}{2\eta b^2} \omega . \xi . \sum_{n=1}^{n=\infty} \sum_{m=0}^{m=n-1} \xi^{2n} \omega^{2m} \cos\{2(n-m)\delta - 4n\psi + \phi\},$$

where we have rewritten the expressions (38) in terms of the abbreviated symbols defined by equations (36), (41), and (42). Carrying out the summation first with regard to $m$,

$$I_2'' = \frac{A^2 . c^2 f^2}{2\eta b^2} \frac{\omega\xi}{1 - 2\omega^2 \cos 2\delta + \omega^4}$$

$$\times \sum_{n=1}^{n=\infty} \xi^{2n} [\cos(2n\delta - 4n\psi + \phi) - \omega^{2n} \cos(4n\psi - \phi)$$

$$- \omega^2 \cos(\overline{2n+2}\delta - 4n\psi + \phi) + \omega^{2n+2} \cos(4n\psi - \phi - 2\delta)].$$

The first and third terms in the square bracket may be summed together, and also the second and fourth. Bringing the two fractions thus obtained to a common denominator, $(1 - 2\omega^2 \cos 2\delta + \omega^4)$ divides out, as in the case of $I_2'$, and we obtain as our final value of $I_2''$

$$I_2'' = \frac{A^2 . c^2 f^2}{2\eta . b^2} \frac{\omega\xi}{1 - 2\omega^2\xi^2 \cos 4\psi + \omega^4\xi^4}$$

$$\times \frac{\left\{ \begin{array}{l} \xi^2 \cos(2\delta + \phi - 4\psi) - \xi^4 \cos\phi \\ - \omega^2\xi^4 \cos(2\delta + \phi) + \omega^2\xi^6 \cos(\phi + 4\psi) \end{array} \right\}}{1 - 2\xi^2 \cos(2\delta - 4\psi) + \xi^4} . \quad (46)$$

Combining (44) (45) and (46) we have the total value of $I_t$, the intensity of the transmitted ray,

$$I_t = I_1 + I_2 = I_1 + I_2' - I_2''$$

$$= \frac{A^2 . c^2 f^2}{4\eta b^2} \omega\xi \left\{ \frac{\sec\chi (1 - \xi^4)}{(1 - 2\xi^2 \cos 2\delta + \xi^4)(1 - \omega^2\xi^2)} \right.$$

$$\left. - \frac{\left\{ \begin{array}{l} (1 - \xi^4)[\cos\phi - \omega^2\xi^2 \cos(\phi + 4\psi)] \\ - 2\xi^2 \sin(2\delta - 4\psi)[\sin\phi - \omega^2\xi^2 \sin(\phi + 4\psi)] \end{array} \right\}}{(1 - 2\omega^2\xi^2 \cos 4\psi + \omega^4\xi^4)(1 - 2\xi^2 \cos(2\delta - 4\psi) + \xi^4)} \right\} . \quad (47)$$

But we want to compare this with the intensity of the ray transmitted when there is no intervening layer of electrolyte.

Calling the intensity of this ray $I_0$, we have for its value

$$I_0=A^2\int_0^\infty e^{-2p_1t}\sin^2p_2t\,.\,dt=\frac{A^2}{4\eta}(\sec\chi-\cos\chi).\quad .\quad (48)$$

Dividing (47) by (48),

$$\frac{I_t}{I_0}=\frac{c^2f^2\,.\,\omega\xi}{b^2(\sec\chi-\cos\chi)}\left\{\frac{(1-\xi^4)\sec\chi}{(1-2\xi^2\cos 2\delta+\xi^4)(1-\omega^2\xi^2)}\right.$$
$$\left.-\frac{\left\{\begin{array}{l}(1-\xi^4)[\cos\phi-\omega^2\xi^2\cos(\phi+4\psi)]\\ -2\xi^2\sin(2\delta-4\psi)[\sin\phi-\omega^2\xi^2\sin(\phi+4\psi)]\end{array}\right\}}{(1-2\omega^2\xi^2\cos 4\psi+\omega^4\xi^4)(1-2\xi^2\cos(2\delta-4\psi)+\xi^4}\right\}.\quad (49)$$

This formula is one of considerable generality, showing the variation in the intensity of the ray transmitted through a thin absorbent plate when the incident ray is logarithmically damped. Two special cases are of interest: (1) when the plate is not conducting; (2) when the incident ray is not damped. Taking the first case,

$$\left.\begin{array}{lll}\text{if}\quad \alpha_2=0, & \psi=\psi'=0, & \delta=p_2t_2,\\ \theta=0, & \rho=1, & \omega\xi=b^2,\\ \xi=be^{-p_1t_2}, & c^2f^2=(1-b^2)^2, & \end{array}\right\}\quad .\quad .\quad (50)$$

and the expression for $\dfrac{I_t}{I_0}$ simplifies to

$$\frac{I_t}{I_0}=\frac{1-b^2}{1+b^2}\left[\frac{1-\xi^4+2\xi^2\sin 2\delta\cot\chi}{1-2\xi^2\cos 2\delta+\xi^4}\right].\quad .\quad .\quad (51)$$

This case was recently worked out by Dr. Barton, and our equation (51) may be reduced to his. Dividing out by the denominator in the square bracket, we get

$$\frac{I_t}{I_0}=\frac{1-b^2}{1+b^2}\left[1-\frac{2\xi^2(\xi^2-\cos 2\delta-\cot\chi\sin 2\delta)}{1-2\xi^2\cos 2\delta+\xi^4}\right].$$

Dr. Barton's expression is*

$$\frac{I_t}{I_0}=\frac{1-b^2}{1+b^2}\left[1+2b^2e^{-\alpha t_2}\frac{(\alpha/\beta)\sin\beta t_2+\cos\beta t_2-b^2e^{-\alpha t_2}}{1-2b^2e^{-\alpha t_2}\cos\beta t_2+b^4e^{-2\alpha t_2}}\right],$$

which is equivalent to ours; his $t_2$ being equal to twice our $t_2$, and his $\alpha/\beta$ equivalent to our $p_1/p_2$ or $\cot\chi$.

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* Proc. Roy. Soc. vol. liv. p. 92; 'Thesis,' p. 13.

As a second special case, suppose we are dealing with a steady simple harmonic ray instead of a damped wave-train. $\chi$ is then ninety degrees, and the other symbols take the special values

$$\left.\begin{array}{l} \chi=90^\circ \quad . \quad \sec\chi=\infty, \\ p_1=0, \quad \therefore \ \omega=\xi=be^{\kappa d}, \\ \rho=\sqrt{1+\left(\dfrac{\alpha^2}{p_2\beta_2}\right)^2}. \end{array}\right\} \quad . \quad . \quad . \quad . \quad (52)$$

The long second term in (49) vanishes altogether now, being divided by $(\sec\chi-\cos\chi)$, and

$$\frac{\mathrm{I}_t}{\mathrm{I}_0}=\frac{c^2f^2}{b^2}\frac{\xi^2}{1-2\xi^2\cos 2\delta+\xi^4}. \quad . \quad . \quad . \quad (53)$$

If in this case we again put $\alpha_2=0$, we have

$$\omega=\xi=b,$$

$$\delta=p_2t_2\,;$$

and so if the plate be a non-conductor,

$$\frac{\mathrm{I}_t}{\mathrm{I}_0}=\frac{c^2f^2}{1-2b^2\cos 2p_2t_2+b^4}, \quad . \quad . \quad . \quad . \quad (54)$$

which is the ordinary expression for the ray transmitted through a thin plate.

The general expression (49) is too complex to allow of an offhand statement of its form. One case was, however, worked out in full arithmetically. The values of the chief constants chosen were

$$\frac{\beta_2}{\beta_1}=70,$$

sp. resistance of electrolyte = 5100 ohm-centim.,

log. decrement of wave-train = 0·4,

wave-length $=\lambda_1=$ 9 metres.

These gave the following values for some of our symbols :—

$$\chi=86^\circ\ 21'\ 26'',$$

$$\theta=\ 8^\circ\ 44'\ 57'',$$

$$\kappa d = -\frac{d}{\lambda_1}(\cdot 673402),$$

$$p_1 t_2 = 3\cdot 3676\,\frac{d}{\lambda_1},$$

$$p_2 t_2 = 3017^\circ\cdot 825\,\frac{d}{\lambda_1},$$

$$b = \cdot 78705, \quad cf = \cdot 38167,$$

$$\log \xi = \bar{1}\cdot 8960008 - \frac{d}{\lambda_1}(3\cdot 21751421),$$

$$\log \omega\xi = \bar{1}\cdot 9920016 - \frac{d}{\lambda_1}(3\cdot 5099681),$$

$$\psi = 1^\circ\ 3'\ 26'', \quad \psi' = 28'\ 17'',$$

$$\rho = 1\cdot 0018.$$

The phase-changes at both surfaces are in this case so small that one would not expect any great shifting of the maxima in the transmission-curve, (1) (fig. 3): the maxima appear to occur rather early, but one can hardly say more. I find (49) too complex to get anything out of it by differentiation.

## V. *The Intensity of the Reflected Ray.*

We will now proceed to calculate the intensity of the reflected ray. As before, let the incident wave be

$$\mathrm{A}\, e^{p(t-\sqrt{\beta_1}z)}.$$

A portion of this incident wave is at once reflected, namely

$$\mathrm{Y} = \mathrm{A}\,.\,b\,.\,e^{p(t+\sqrt{\beta_1}z)}\,e^{-i\psi}. \quad . \quad . \quad . \quad . \quad . \quad (55)$$

A second portion enters the electrolyte and reaches the second surface in the form

$$\mathrm{A}\,.\,c\,.\,e^{p(t-qd)}\,e^{i(\theta/2-\psi')},$$

is there reflected, reaches the first surface again and emerges at time $2t_2$,

$$y_1 = -\mathrm{A}\,.\,bcf\,.\,e^{-2pqd}\,e^{p(t+\sqrt{\beta_1}z)}\,e^{i(\theta/2-2\psi'-\psi)}.$$

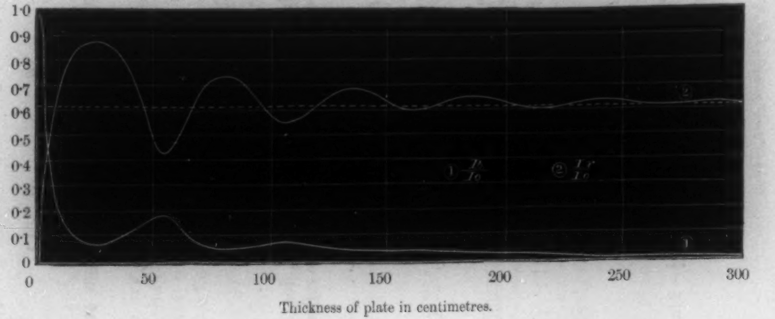
The next wave emerges after three internal reflexions at time $4t_2$,

$$y_2 = -\mathrm{A}\,.\,b^3cf\,.\,e^{-4pqd}\,e^{p(t+\sqrt{\beta_1}z)}\,e^{i(\theta/2-2\psi'-3\psi)},$$

Fig. 3.

Curves showing the variation of $\frac{I_t}{I_0}$ and $\frac{I_r}{I_0}$ with the thickness of the plate.

Ratio of dielectric constants $= \frac{\beta_2}{\beta} = 70$. Sp. resistance of plate 5100 ohm-centim.



and so on ; the expression for the wave emergent at time $2nt_2$ being

$$y_n = -\mathrm{A} \,.\, b^{2n-1}\, cf \,.\, e^{-2npqd}\, e^{p(t+\sqrt{\beta_1}x)}\, e^{i(\theta/2-2\psi)}\, e^{i(2n-1)\psi} . \quad . \quad (56)$$

Now

$$pq = \eta\sqrt{\beta_2\rho}\left[i\sin\left(\frac{\theta}{2}+\chi\right) - \cos\left(\frac{\theta}{2}+\chi\right)\right].$$

Inserting this value in (56), and using our previous abbreviations,

$$\kappa = \eta\sqrt{\beta_2\rho}\cos\left(\frac{\theta}{2}+\chi\right), \quad \alpha = \left(\frac{\theta}{2} - 2\psi' + \psi\right), \quad . \quad (33)$$

$$\delta = p_2 t_2 + \psi, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

and retaining only the sine terms, we have

$$y_n = -\mathrm{A}\, cf b^{2n-1}\, e^{2n\kappa d}\, e^{-p_1 t} \sin(p_2 t + \alpha - 2n\,\delta). \quad . \quad (57)$$

It is to be noted that the first reflected wave, Y, does not fall into this series so the general expression for the reflected intensity will be

$$\mathrm{I}_r = \mathop{\mathrm{S}}_{n=1}^{n=\infty} \int_{2nt_2}^{\infty} y_n^2\,dt + 2 \mathop{\mathrm{S}}_{m=1}^{m=n-1} \mathop{\mathrm{S}}_{n=2}^{n=\infty} \int_{2nt_2}^{\infty} y_m y_n\,dt$$
$$+ \int_0^{\infty} \mathrm{Y}^2\,dt + 2\mathop{\mathrm{S}}_{n=1}^{n=\infty} \int_{2nt_2}^{\infty} \mathrm{Y}\, y_n\,dt. \quad . \quad . \quad (58)$$

Multiplying out $y_m y_n$ we get

$$y_m y_n = \tfrac{1}{2}\mathrm{A}^2 c^2 f^2 b^{2(m+n-1)}\, e^{2(m+n)\kappa d}\, e^{-2p_1 t}$$
$$\times\{\cos 2(m-n)\delta - \cos[2(p_2 t+\alpha) - 2(m+n)\delta]\} ; \quad (59)$$

and integrating from $t=2nt_2$ to $t=\infty$,

$$\int_{2nt_2}^{\infty} y_m y_n\,dt = \frac{1}{4\eta}\mathrm{A}^2 c^2 f^2 b^{2(m+n-1)}\, e^{2(m+n)\kappa d}$$
$$\times e^{-4np_1t_2}\left\{\frac{\cos 2(m-n)\delta}{\cos\chi} - \cos[2(n-m)p_2t_2 + 2\alpha + \chi] - 2(n+m)\psi\right\} \quad (60)$$

Putting $m=n$,

$$\int_{2nt_2}^{\infty} y_n^2\,dt = \frac{1}{4\eta}\mathrm{A}^2 c^2 f^2 b^{4n-2}\, e^{4n\kappa d}\, e^{-4np_1t_2}$$
$$\times\{\sec\chi - \cos(2\alpha + \chi - 4n\psi)\}. \quad . \quad . \quad (61)$$

The summation of (61) from $n=1$ to $n=\infty$ is performed in exactly the same way as that of the analogous expression for $I_t$ in equations (39) to (44). The result is

$$\underset{n=0}{\overset{n=\infty}{S}} \int_{2nt_2}^{\infty} y_n^2 dt = \frac{A^2c^2f^2}{4\eta b^2}\,\omega^2\xi^2$$

$$\times\left\{\frac{\sec\chi}{1-\omega^2\xi^2} - \frac{\cos(\phi-2\psi)-\omega^2\xi^2\cos(\phi+2\psi)}{1-2\omega^2\xi^2\cos 4\psi+\omega^4\xi^4}\right\}. \quad (62)$$

The summation of the product integrals in (60) is also analogous to that of the product integrals in $I_t$ given in equations (44) to (46). Taking the integral in two parts as before, we have for the sum of the terms containing $\sec\chi$ :—

$$\frac{A^2c^2f^2}{2\eta b^2}\,\omega^2\xi^2\sec\chi\,\frac{\xi^2(\cos 2\delta-\xi^2)}{(1-\omega^2\xi^2)(1-2\xi^2\cos 2\delta+\xi^4)}\,; \quad (63)$$

and for the sum of the second terms, those not containing $\sec\chi$ :—

$$\left.\begin{aligned}&\frac{A^2c^2f^2}{2\eta b^2}\,\frac{\omega^2\xi^2}{1-2\omega^2\xi^2\cos 4\psi+\omega^4\xi^4}\\ &\times\frac{\xi^2\cos(2\delta-6\psi+\phi)-\xi^4\cos(\phi-2\psi)-\omega^2\xi^4\cos(2\delta-2\psi+\phi)\,[+\omega^2\xi^6\cos(2\psi+\phi)}{1-2\xi^2\cos 2\delta+\xi^4}\end{aligned}\right\}(64)$$

Adding together (62) (63) and (64), bringing the second half of (62) and (64) to a common denominator and simplifying, we get the expression for that portion of $I_r$ which is a function of the uniform series of $y$'s only. Calling it $I'_r$, and dividing out by $I_0$ the "intensity" of the incident ray, we get :—

$$\frac{I'_r}{I_0} = \frac{c^2f^2\,.\,\omega^2\xi^2}{b^2(\sec\chi-\cos\chi)}\left\{\frac{(1-\xi^4)\sec\chi}{(1-2\xi^2\cos 2\delta+\xi^4)(1-\omega^2\xi^2)}\right.$$

$$-\frac{(1-\xi^4)\{\cos(\phi-2\psi)-\omega^2\xi^2\cos(\phi+2\psi)\}}{(1-2\omega^2\xi^2\cos 4\psi+\omega^4\xi^4)}$$

$$\left.\frac{-2\xi^2\sin(2\delta-4\psi)\{\sin(\phi-2\psi)-\omega^2\xi^2\sin(\phi+2\psi)\}}{(1-2\xi^2\cos(2\delta-4\psi)+\xi^4)}\right\},(65)$$

an expression very similar to that for $I_t/I_0$ given in equation (49). Reverting now to the terms containing Y in (58), let us evaluate

$$2\overset{n=\infty}{\underset{n=1}{\mathrm{S}}}\int_{2nt_2}^{\infty}\mathrm{Y}\,.\,y_n\,dt.$$

Rationalizing (55) we have

$$\mathrm{Y}=\mathrm{A}b\,.\,e^{-p_1t}\sin(p_2t-\psi). \quad . \quad . \quad . \quad . \quad (66)$$

The expression for $y_n$ is given in (56) : multiplying up

$$\mathrm{Y}y_n=-\tfrac{1}{2}\mathrm{A}^2cf\omega^2{}_ne^{-2p_1t}[\cos(2n\delta-\alpha-\psi)-\cos(2p_2t+\alpha-\psi-2n\delta)].$$

Integrating from $2nt_2$ to infinity, and writing for brevity

$$\Delta=\alpha-\psi+\chi, \quad . \quad . \quad . \quad . \quad . \quad . \quad (67)$$

we get

$$\int_{2nt_2}^{\infty}\mathrm{Y}y_n\,dt=-\mathrm{A}^2\,.\,\frac{cf}{4\eta}\,.\,\xi^{2n}$$

$$\times\,[\sec\chi\,.\cos(2n\delta-\alpha-\psi)-\cos\{2n(p_2t_2-\psi)+\Delta\}].$$

Summing this from $n=1$ to $n=\infty$, and multiplying by two,

$$2\overset{n=\infty}{\underset{n=1}{\mathrm{S}}}\int_{2nt_2}^{\infty}\mathrm{Y}\,.\,y_n\,dt=-\mathrm{A}^2\frac{cf}{2\eta}\,.\,\xi^2$$

$$\times\left[\frac{\sec\chi\{\cos(2\delta-\alpha-\psi)-\xi^2\cos(\psi+\alpha)\}}{1-2\xi^2\cos2\delta+\xi^4}\right.$$

$$\left.-\frac{\cos(\Delta+2\delta-4\psi)-\xi^2\cos\Delta}{1-2\xi^2\cos(2\delta-4\psi)+\xi^4}\right]. \quad . \quad (68)$$

Calling this $\mathrm{I}''_r$, and dividing through by $\mathrm{I}_0$ we get

$$\frac{\mathrm{I}''_r}{\mathrm{I}_0}=\frac{-2cf\,.\,\xi^2}{\sec\chi-\cos\chi}\left\{\frac{\sec\chi\{\cos(\psi+\alpha-2\delta)-\xi^2\cos(\psi+\alpha)\}}{1-2\xi^2\cos2\delta+\xi^4}\right.$$

$$\left.-\frac{\cos(\Delta+2\delta-4\psi)-\xi^2\cos\Delta}{1-2\xi^2\cos(2\delta-4\psi)+\xi^4}\right\}. \quad . \quad (69)$$

The remaining portion of $\mathrm{I}_r$ is

$$\mathrm{I}'''_r=\int_0^{\infty}\mathrm{Y}^2\,dt=\int_0^{\infty}\mathrm{A}^2b^2e^{-2p_1t}\sin^2(p_2t-\psi)dt$$

$$=\frac{\mathrm{A}^2b^2}{4\eta}\{\sec\chi-\cos(\chi-2\psi)\}.$$

Dividing out by $I_0$,

$$\frac{I'''_r}{I_0} = \frac{b^2[\sec\chi - \cos(\chi - 2\psi)]}{\sec\chi - \cos\chi} \qquad (70)$$

This last expression is independent of the thickness of the slab of electrolyte.

The total expression for $\frac{I_r}{I_0}$ is (65) + (69) + (70), or rewriting these equations,

$$\begin{aligned}\frac{I_r}{I_0} = \frac{c^2 f^2 . \omega^2\xi^2}{b^2(\sec\chi - \cos\chi)}\Bigg\{&\frac{(1-\xi^4)\sec\chi}{(1-2\xi^2\cos 2\delta+\xi^4)(1-\omega^2\xi^2)}\\ &-\frac{\left\{\begin{array}{l}(1-\xi^4)[\cos(\phi-2\psi)-\omega^2\xi^2\cos(\phi+2\psi)]\\ -2\xi^2\sin(2\delta-4\psi)[\sin(\phi-2\psi)-\omega^2\xi^2\sin(\phi+2\psi)]\end{array}\right\}}{(1-2\omega^2\xi^2\cos 4\psi+\omega^4\xi^4)(1-2\xi^2\cos(2\delta-4\psi)+\xi^4)}\Bigg\}\\ -2\frac{cf.\xi^2}{\sec\chi-\cos\chi}\Bigg\{&\frac{\sec\chi[\cos(\psi+\alpha-2\delta)-\xi^2\cos(\psi+\alpha)]}{1-2\xi^2\cos 2\delta+\xi^4}\\ &-\frac{\cos(\Delta+2\delta-4\psi)-\xi^2\cos\Delta}{1-2\xi^2\cos(2\delta-4\psi)+\xi^4}\Bigg\}\\ +\frac{b^2[\sec\chi-\cos(\chi-2\psi)]}{\sec\chi-\cos\chi}& \qquad (71)\end{aligned}$$

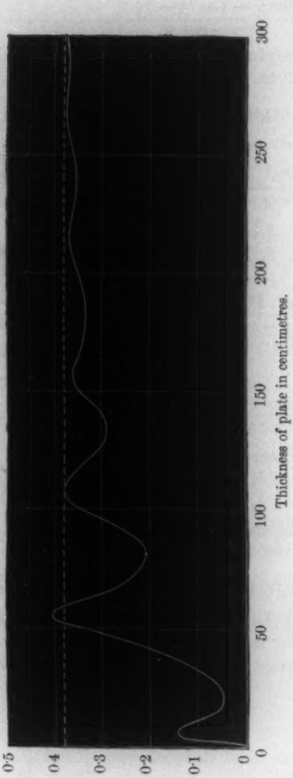
As a matter of arithmetic this expression is fairly quickly calculable if $\frac{I_t}{I_0}$ has been already worked out; a large number of the constants, &c., are the same in the two cases. The curve (2) (fig. 3) has been calculated from the same data as were given on p. 376; the two curves $\frac{I_t}{I_0}$ and $\frac{I_r}{I_0}$ may be thus compared. In the former the maxima were slightly shifted back, in the latter the minima are slightly shifted forward. The proportion of energy absorbed by the plate is

$$1 - \left(\frac{I_t + I_r}{I_0}\right).$$

The curve thus deduced from $\frac{I_t}{I_0}$ and $\frac{I_r}{I_0}$ is shown in fig. 4. As $\frac{I_t}{I_0}$ asymptotes to zero, and $\frac{I_r}{I_0}$ asymptotes to $\frac{I'''_r}{I_0}$ (70), $\left\{1 - \frac{I_t + I_r}{I_0}\right\}$ asymptotes towards the value $1 - I'''_r/I_0$; that is

Fig. 4.

Curve showing the variation in the energy absorbed by the plate $= 1 - \frac{I_t + I_r}{I_0}$.



to say, when the layer of electrolyte gets very thick all is absorbed but the ray reflected from the first surface.

The expression for $\frac{I_r}{I_0}$ given in (71) may be checked by putting $a_2$ zero. Taking the three parts (65) (69) (70) separately, the first becomes at once

$$b^2\frac{I}{I_0},$$

where $\frac{I_t}{I_0}$ is the expression given in (51) or the following equation. The second part reduces to

$$(1-b^2)\frac{2\xi^4-2\xi^2\cos 2\delta-2\xi^2\sin 2\delta\,.\cot\chi}{1-2\xi^2\cos 2\delta+\xi^4}=1-b^2-(1+b^2)\frac{I_t}{I_0}.$$

The third part gives simply $b^2$. Adding up we get

$$\left(\frac{I_r}{I_0}\right)_{a_2=0}=b^2\frac{I_t}{I_0}+1-b^2-(1+b^2)\frac{I_t}{I_0}+b^2$$

$$=1-\left(\frac{I_t}{I_0}\right)_{a_2=0}.$$

The expression for $\frac{I_r}{I_0}$ also becomes greatly simplified if we take the incident ray to be non-damped. In this case

$$\sec\chi=\infty,\quad \omega=\xi=be^{\kappa d}$$

as before, and

$$\frac{I_r}{I_0}=\frac{c^2f^2}{b^2}\frac{\xi^4}{1-2\xi^2\cos 2\delta+\xi^4}$$

$$-2cf\,.\,\xi^2\,.\,\frac{\cos(\psi+a-2\delta)-\xi^2\cos(\psi+a)}{1-2\xi^2\cos 2\delta+\xi^4}$$

$$+b^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (71a)$$

If we now put $a_2=0$, we have $\omega=\xi=b$, and $\delta=p_2t_2$, and so on, as given on p. 375, and the expression becomes

$$\frac{I_r}{I_0}=\frac{c^2f^2b^2}{1-2b^2\cos 2p_2t_2+b^4}$$

$$- 2cfb^2 \frac{\cos 2p_2t_2 - b^2}{1 - 2b^2 \cos 2p_2t_2 + b^4}$$

$$+ b^2$$

$$= \frac{2b^2(1 - \cos 2p_2t_2)}{1 - 2b^2 \cos 2p_2t_2 + b^4}, \quad . \quad . \quad . \quad . \qquad (71\,b)$$

which is the ordinary expression for 'Newton's Rings by Reflexion.'

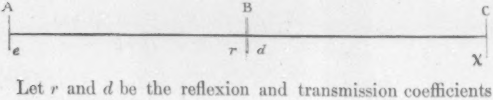
## VI. *Discussion of an Experimental Case and a Correction.*

This section is independent of the rest of the paper, being devoted to the discussion of a correction necessary in the experimental case mentioned at the beginning.

It has been stated already in the introduction that the theory, sections IV. & V., does not give numerical results agreeing closely with the experimental ones. For all the values of $\beta_2/\beta_1$ I tried, the calculated points lay continually below the experimental determinations. Dr. Barton found exactly the same peculiarity in his analogous experiments, and suggested that it might be due to the coursing of the wave-trains backwards and forwards along the wire circuit between the oscillator and the closed end. Working from this idea he arrived at a correction formula*, which, however, is not immediately applicable to our case. The following analysis is equivalent to Dr. Barton's though differing in method.

Let ABC (fig. 5) represent our circuit, B being the electrolyte, A the oscillator, C the closed end.

Fig. 5.



Let $r$ and $d$ be the reflexion and transmission coefficients at the electrolyte, with regard to energy, so that

$$I_t = tI_0, \quad I_r = rI_0.$$

Let $e$ and $\chi$ be similar coefficients for the two halves of the wire circuit—reduction coefficients covering loss of energy due either to damping by the imperfectly conducting wires or to imperfect reflexion at the ends of the circuit.

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* 'Thesis,' p. 16, section V.

If then

$T_n$ is the intensity of the $n^{\text{th}}$ train emerging from B towards C,

$R_n$ is the intensity of the $n^{\text{th}}$ train reflected from B towards A,

we have

$$\left.\begin{aligned} T_{n+1} &= ed\,R_n + r\chi\,T_n \\ R_{n+1} &= d\chi\,T_n + re\,R_n \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The effect on the electrometer is proportional to

$$\mathop{\mathrm{S}}_{n=0}^{n=\infty} (1+\chi)T_n,$$

so we have to sum a finite-difference series.

Let

$$\left.\begin{aligned} T_n &= Ab^n \\ R_n &= Bb^n \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Rewriting (1) with these values of $T_n$ and $R_n$, we have

$$\left.\begin{aligned} Ab &= ed\ B + r\chi\,A, \\ Bb &= d\chi\,A + re\ B, \end{aligned}\right\}$$

whence, eliminating A and B,

$$b^2 - br\,(e+\chi) + e\chi\,(r^2-d^2) = 0. \quad . \quad . \quad . \quad (3)$$

This is an equation to determine $b$. Suppose $b_1$ and $b_2$ to be the roots; $A_1$ $A_2$, $B_1$ $B_2$ being the corresponding values of A and B. We have then

$$b_1 + b_2 = r(e+\chi), \quad b_1 b_2 = (r^2-d^2)\,e\chi. \quad . \quad . \quad . \quad (4)$$

$$\left.\begin{aligned} T_n &= A_1 b_1^n + A_2 b_2^n \\ R_n &= \frac{d\chi}{b_1 - re}\,A_1 b_1^n + \frac{d\chi}{b_2 - re}\,A_2 b_2^n \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

From this last equation,

$$\left.\begin{aligned} T_0 &= dI_0 = A_1 + A_2, \\ R_0 &= rI_0 = d\chi\left(\frac{A_1}{b_1 - re} + \frac{A_2}{b_2 - re}\right), \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (6)$$

The total effect on the electrometer is consequently proportional to E where

$$E=(1+\chi)\overset{\infty}{\underset{0}{S}}\,T_n=(1+\chi)\left\{\frac{A_1}{1-b_1}+\frac{A_2}{1-b_2}\right\}$$

$$=(1+\chi)\left\{\frac{A_1+A_2-(b_2A_1+b_1A_2)}{1-(b_1+b_2)+b_1b_2}\right\}.$$

And from (6),

$$rI_0=d\chi\left\{\frac{b_2A_1+b_1A_2-re(A_1+A_2)}{b_1b_2-re(b_1+b_2)+r^2e^2}\right\}.$$

But by the relations (4),

$$1-(b_1+b_2)+b_1b_2=1-r(e+\chi)+e\chi\,(r^2-d^2),$$

$$b_1b_2-re(b_1+b_2)+r^2e^2=-e\chi d^2,$$

whence

$$-edrI_0=b_2A_1+b_1A_2-red\,I_0,$$

or

$$b_2A_1+b_1A_2=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Thus, finally,

$$E=(1+\chi)\frac{dI_0}{1-r(e+\chi)+e\chi(r^2-d^2)},$$

$$E_0=(1+\chi)\frac{I_0}{1-e\chi},$$

and

$$\frac{E}{E_0}=\frac{(1-e\chi)d}{1-r(e+\chi)+e\chi(r^2-d^2)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$\frac{E}{E_0}$ is an ordinate of the experimental curve. $d$ and $r$ are ordinates of our calculated transmission and reflexion curves. If then we determine $\frac{E}{E_0}$, $d$, and $r$ for the different thicknesses of the electrolyte, we shall have by substituting their values in (8) a pair of simultaneous equations for the determination of $e$ and $\chi$.

This process only led to impossibilities for all values of $\beta_1/\beta_2$ and the log. dec. of the wave-train that were tried. Either $e\chi$ became greater than unity or negative, or $e+\chi$ became negative.

It may be noted that this correction did not work very successfully in Dr. Barton's case either. His method of applying it was, however, different: having formed an experimental estimate of the rate of decrease of the total energy of a wave-train by its passage along the imperfectly conducting wires, he assumed that there was perfect reflexion at both ends of the circuit, and thence calculated the correction to be applied to the experimental curve. The corrected curve obtained in this way lay below the calculated curve. Taking two points at random on his curves, I tried to calculate $e\chi$ and $e+\chi$ by my method. The results were again impossible.

It must be remembered that in both these cases more than one of the constants of the theoretical curve were simple guesses, $\gamma$ and $\beta_2/\beta_1$ in my case were both only approximately known. In trying to make things square by the correction of (8), we may have been attempting the impossible and rightly got irrational results. I need not dwell at greater length on this point: possible causes of error are numerous. The non-agreement of experimental results with the equations does not of course prove the wrongness of the latter, but only the wrongness of their application to the case.

I am compelled to admit that, considering the positions of the maxima in my experimental curves are dependent on the phase-changes and on the correction we have been discussing —possibly also on other uneliminated disturbances—no great weight can be attached to the accuracy of the values of the dielectric constants for water, alcohol, &c., deduced on the assumption that such corrections were negligible *.

## VII. *The Numerical Value of some of the previous Results.*

When the expressions in sections II. and III. had been obtained, the question at once arose, how far the values of $b$, $c$, $f$, $\psi$, $\psi'$, and so on might be practically affected by possible variations in the rate of damping of the incident ray. In working with ordinary oscillators are changes likely to become important or to remain quite negligible? In working with light are differences likely to be appreciable between flashes and steady rays?

As regards oscillator wave-trains, the damping should certainly be taken into account. The second question, however, must, I think, be answered in the negative, for the simple reason that one cannot get a quick enough flash*. Even an electric spark lasts for thousands or millions of the vibrations of violet light: the rays from it would be practically steady, not damped.

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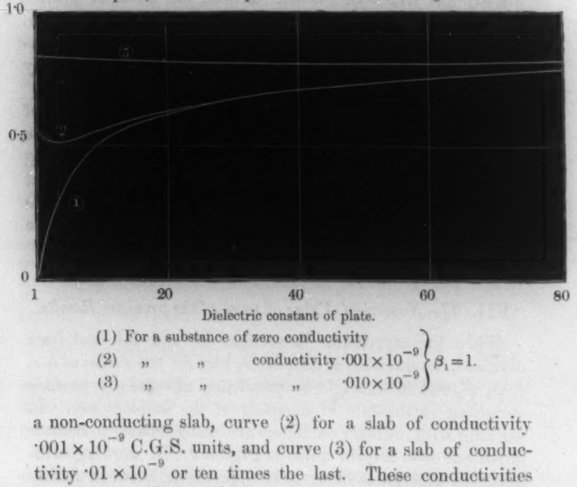
* Phil. Mag. vol. xxxvi. p. 539; Wied. *Ann.* vol. l. p. 748.

The set of curves in fig. 6 is drawn for a steady ray, wave-length one metre. It illustrates the variation in $b$ (the ratio of the transmitted to the incident amplitude at the surface of an infinitely thick slab), when the conductivity and dielectric constant of the slab vary. Curve (1) is drawn for a non-conducting slab, curve (2) for a slab of conductivity $\cdot 001 \times 10^{-9}$ C.G.S. units, and curve (3) for a slab of conductivity $\cdot 01 \times 10^{-9}$ or ten times the last. These conductivities are all extremely low, that of a 5 p. c. copper sulphate or zinc sulphate solution being roughly $\cdot 2 \times 10^{-9}$. The curves show very well how rapidly the conductivity of the reflecting plate

Fig. 6.

Curves showing the variation in "$b$" with the dielectric constant and conductivity of the plate, for an undamped wave-train. Wave-length 100 cms.



$$\left.\begin{array}{llll}(1) & \text{For a substance of zero conductivity} & & \\ (2) & ,, \quad ,, & \text{conductivity} & \cdot 001 \times 10^{-9} \\ (3) & ,, \quad ,, & ,, & \cdot 010 \times 10^{-9}\end{array}\right\} \beta_1 = 1.$$

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* Unless light be itself an aggregate of damped wave-trains.

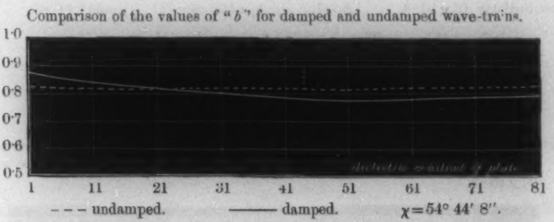
grows in importance relatively to the dielectric constant even for great wave-lengths.

But if we take the case of a charge vibrating on an isolated perfectly conducting sphere, the amplitude falls to $e^{-\frac{2\pi}{\surd}}$ or about $\frac{1}{38}$ of its original value in the time occupied by a complete vibration*: this gives us $\chi = 54° 44' 8''$. Let us use this as an example of a damped wave-train to compare with the steady ray, retaining the same wave-length—1 metre—corresponding to a sphere about a foot in diameter.

The curve (1) for $b$ corresponding to a non-conducting plate would be the same in both cases. The curves (3) corresponding to a plate of conductivity $\cdot 01 \times 10^{-9}$ are shown together in fig. 7. $b$ is at first greatest for the damped wave-train, but as the dielectric constant is increased this ratio is reversed. Physically speaking, this has very little meaning: any actual method would measure the energy of the reflected ray, and it has been shown † that the energy is a function of the phase-change, the phase-change being itself a function of the rate of damping of the wave-train. Taking the phase-changes, $\psi$, first, I calculated them for the steady ray, for the damped ray with which we are dealing, and the conductivity $\cdot 01 \times 10^{-9}$. The results are given together in

Fig. 7.

Comparison of the values of "$b$" for damped and undamped wave-trains.



Conductivity of plate $= \cdot 01 \times 10^{-9}$. Wave-length in either case $= 100$ cms. $\beta_1 = 1$.

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* J. J. Thomson, 'Recent Researches,' p. 370.

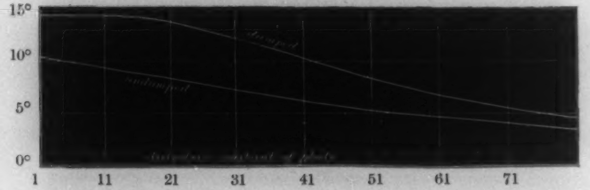
† Equation (70).

fig. 8. For the lower values of the dielectric constant, $\psi$ for the damped wave-train is about half as large again as for the steady ray.

Utilizing these values of $\psi$ for calculating the intensity of the reflected ray, we get the pair of curves in fig. 9. The result is striking. The energy of the reflected waves for the steady ray is from 15–20 p. c. of the incident energy greater than for the damped ray.

Fig. 8.

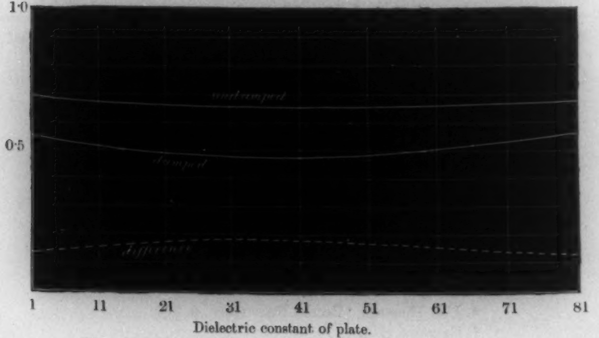
$\psi$ for damped and undamped wave-trains.



Conductivity ·01 × 10−9. $\beta_1 = 1$. $\lambda_1 = 100$ cms. $\chi = 54° 44' 8''$.

Fig. 9.

Curves showing the difference between the intensities of the portions of damped and undamped wave-trains reflected from an infinitely thick plate of conductivity ·01 × 10−9.



Wave-length = 100 cms. $\chi = 54° 44' 8''$. $\beta_1 = 1$.

Experimental evidence for these results would be very interesting; but, so far as I am aware, there is none whatever. In cases where $\chi$ was taken between 80° and 90°, the alterations would be much smaller and more difficult to detect. The curves I have given only illustrate, however, a very small section of cases, even larger variations may be possible.

I am glad to have this opportunity of expressing my indebtedness to Professor Karl Pearson, to whom my best thanks are due for much advice and assistance.

### TABLE *of the principal Symbols used.*

The suffix 1 refers to the dielectric; the suffix 2 to the plate. In our case, where all media are assumed to be non-magnetic,

$\beta$ = dielectric constant,
$a = 4\pi \times$ conductivity.

$b$ = ratio of the reflected to the incident amplitude at the first surface of the plate.

$e$ = the corresponding ratio at the second surface.

$c$ = ratio of the refracted to the incident amplitude at the first surface.

$f$ = the corresponding ratio at the second surface.

$d$ = thickness of slab.

$\lambda_1$ = wave-length in dielectric.

$\lambda_2$ = ,, ,, electrolyte.

$-\psi$ = the change of phase on reflexion at the first surface.

$-\psi'$ = ,, ,, refraction through the second surface.

$p = -p_1 + ip_2$ is defined by (4).

$\eta$, $\chi$ are defined by (9).

$\chi$ gives the rate of damping of the wave-train, being 90° for a steady ray.

$\rho$, $\theta$ are defined by (10).

$r$ is ,, ,, (11).

$\kappa$, $\alpha$ are ,, ,, (33).

$\delta$ is ,, ,, (36).

$\omega$, $\xi$ are ,, ,, (41).

$\phi$ is ,, ,, (42).

$\Delta$ ,, ,, ,, (67).

$$I_t/I_o = \frac{\text{intensity of transmitted ray}}{\text{intensity of incident ray}}.$$

$$I_r/I_o = \frac{\text{intensity of reflected ray}}{\text{intensity of incident ray}}.$$

## Discussion.

A letter from Dr. E. H. **Barton** was read emphasizing the necessity of taking into account the damping in the oscillator-train, and at the same time pointing out why, in his opinion, the corrections applied by Mr. Yule were inadequate and failed to yield intelligible results.

Prof. **Rücker** congratulated Mr. Yule on his work, and on the importance of the results he had obtained.

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## XXXIV. *Energy Movements in the Medium separating Electrified or Gravitating Particles.* *By* H. N. Allen, *University of Nebraska, Lincoln, Neb.*[*]

1. Faraday and Maxwell have shown that it is possible to look on the potential energy of electric separation as residing in the surrounding dielectric, and that each of the cells, bounded by the walls of a tube of force and two neighbouring equipotential surfaces, can be looked upon as containing a certain definite amount of energy.

This energy-distribution is not in general permanent, and can only be regarded as a step towards some simpler arrangement. Thus a positive and a negative electrified body suspended in space, and acted on only by the electrical forces between them, are never in equilibrium until they are in actual contact. The energy-distribution in the dielectric changes constantly as they approach. Poynting has shown[†] how energy is transferred from one point to another in an electromagnetic field; and we are quite accustomed to think of energy as flowing from dynamo to motor through the æther, or from primary to secondary in an alternating-current transformer.

In the following pages an attempt is made to deduce a few of the consequences of Maxwell's suggestion with regard to energy-distribution. The changes needed in the theory in order to apply it to gravitation are also indicated.

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[*] Read March 8, 1895.

[†] Phil. Trans. 1884, Pt. II. p. 343.

2. If two equal charges of positive and negative electricity $+\mathrm{M}$ and $-\mathrm{M}$ are separated by a distance $l$, the equation to the curve in which the equipotential surface V intersects the plane of the paper is

$$\frac{\mathrm{M}}{\sqrt{y^2+(\frac{1}{2}l-x)^2}}-\frac{\mathrm{M}}{\sqrt{y^2+(\frac{1}{2}l+x)^2}}=\mathrm{V}, \quad . \quad (1)$$

the origin being the point midway between the particles, and the X-axis being the line joining this point to the positive particle.

3. The number of tubes of force proceeding from a charge M has sometimes been taken as M but more generally as $4\pi\mathrm{M}$. For graphical methods the former plan seems most convenient, and in order to avoid confusion it is proposed that the resulting tubes should be called "tubes of polarization," while the smaller tubes retain the name "tubes of induction." The polarization, as defined by J. J. Thomson in his 'Recent Researches in Electricity and Magnetism,' is measured by the number of these polarization tubes which pass through a square centimetre perpendicular to their direction.

Using Maxwell's method of drawing the boundary lines between the tubes of polarization, the equation to the $n^{\text{th}}$ line in the case mentioned above will be

$$\frac{\frac{1}{2}l-x}{\sqrt{y^2+(\frac{1}{2}l-x)^2}}+\frac{\frac{1}{2}l+x}{\sqrt{y^2+(\frac{1}{2}l+x)^2}}=2-\frac{2n}{\mathrm{M}}, \quad . \quad (2)$$

where the straight line drawn from the positive to the negative particle is called zero, and that drawn in the opposite direction M.

4. The point of intersection of the equipotential surface V, the line of force $n$, and the plane of the paper lies on the curves (1) and (2). If, then, $l$ in these equations be regarded as a variable parameter, they will together represent the curve along which the corner of an energy-cell moves, when the two particles come together. To plot this curve, the equipotential surfaces and lines of force might be drawn for a number of different distances between the particles, and corresponding points of intersection joined.

The path of the energy-cell can be obtained with less labour from measures made on a single diagram, drawn to represent the lines of force and equipotential surfaces about the two particles, when these are separated by a given distance. This is done by taking advantage of the following properties of these lines :—

1. When the distance between the particles is changed, corresponding tubes of polarization in the two diagrams are similar to one another.

2. The equipotential surfaces in the two diagrams are also similar to one another. If, however, the distance between the particles changes from $l$ to $al$, the equipotential surface V changes to a similar surface, on which the potential is $\frac{V}{a}$.

If, then, the $n^{\text{th}}$ line of force cuts the equipotential surface V at the point $x$, $y$ in the first diagram, the $n^{\text{th}}$ line will cut the equipotential surface $\frac{V}{a}$ at the point $ax$, $ay$ in the second diagram.

Thus, in the case where $M=12$ and $l=10$ the coordinates of the following intersections, among others, were found by measurement on a carefully prepared diagram.

| Line of force. | Equipotential surface. | $x$. | $y$. |
|---|---|---|---|
| 7 | 1 | 5·15 | 5·95 |
| 7 | 4 | 5·35 | 2·28 |

If the diagram were enlarged in the ratio of 4 to 1, the coordinates of the point corresponding to the intersection of 7 and 4 would be $4x$ and $4y$ or 21·4 and 9·12.

The potential at this point would be $V'=\frac{V}{a}=1$.

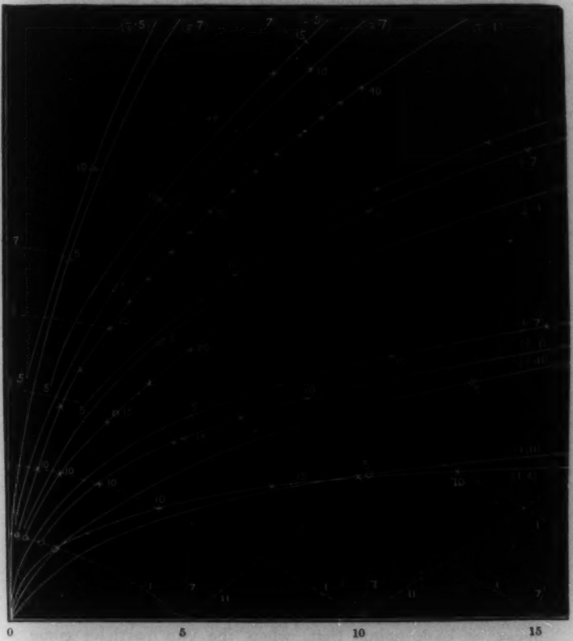
Thus we have found the coordinates of the point of intersection of the line of force 7 and the equipotential surface 1, when the distance between the particles is 40 centim.

In the same way, and by means of the same original diagram, the point of intersection can be found for a number of other distances, and the path which it follows, when the two particles approach one another, can be plotted as in fig. 1.

In this figure the first of the numbers in brackets attached to each curve gives the number of the equipotential surface, and the second that of the intersecting line of force. The numbers along the curves show the distance of the particles from the centre of gravity, when the energy-cell is at the point marked on the curve.

It will be seen that the energy-cells move in more or less

Fig. 1.

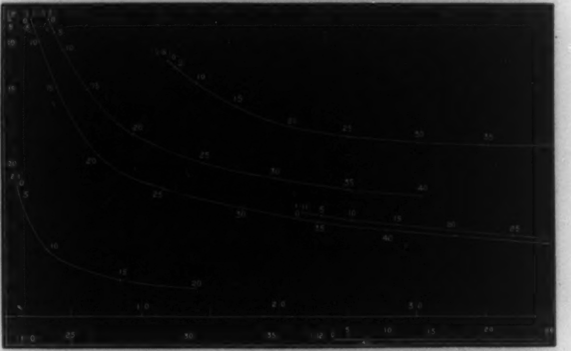


parabolic curves towards the centre of gravity of the two particles, and that during this process they are constantly approaching the two particles; so that, if these are not infinitely small, energy must be constantly passing into them from the æther.

Maxwell has shown that in all cases the number of energy-cells in the æther is twice the potential energy of the system. So that, if we suppose each cell to contain half a unit of energy, we may regard them as preserving their identity when the bodies approach, and as being absorbed by the moving bodies, so that their potential energy is converted into kinetic. A conductor moves in such a way that the absorbed energy is a maximum.

Fig. 1 also illustrates the rotation of the energy-cell as the particles approach. If on any one of the energy-paths, as for instance ($\frac{1}{2}$ . 7), the direction of the line of force (indicated by a dotted line) cutting it at different points be noticed, it will be seen that this direction constantly changes as the particles approach, so that the tangent to the line of force rotates about the point of intersection. The velocity of the different energy-cells is indicated by crosses along the curves, at such points that, when the two particles come together from an infinite distance apart, the cells move from cross to cross in equal intervals of time. The same time is taken in moving from the cross marked 10 to the origin.

Fig. 2.



5. In fig. 2 the paths of the energy-cells are shown when two equal like particles repel one another. It will be noticed

that, as the particles move apart, the energy in each half of the field follows the motion of the particle in that half, and at the same time moves nearer to the central line.

It is clear that the result will be that energy will flow from the dielectric into the particle as it moves away, and being lost as potential energy will reappear as energy of motion. Even when the particles are an infinite distance apart there will still be a number of energy-cells in the æther, that is, the particles will still possess potential energy.

This is explained by supposing that every polarization tube must begin and end somewhere. In this case we may suppose that though A and B are an infinite distance apart, the negative particle C is again an infinite distance beyond A, and the negative particle D an infinite distance beyond B, so that the tubes from A end in C, and those from B in D. Then, after B and A have been repelled to a great distance from one another and all the potential energy due to their original nearness has been exhausted, there will still remain the energy due to the separation of D from B and of A from C.

6. If $H_e$ is the intensity of the electrostatic field, or the force acting upon a particle with unit charge;
$B_e$ the number of tubes of induction per sq. centim., or the induction in the direction of the line of force;
$D_e$ the number of polarization tubes per sq. centim., or the polarization or displacement in the same direction;
K the dielectric constant of the medium;

we have $H_e = \frac{B_e}{K}$, $D_e = \frac{KH_e}{4\pi} = \frac{B_e}{4\pi}$.

The length of an energy-cell is $\frac{1}{H_e}$ or $\frac{K}{4\pi D_e}$.

The area of section of the cell is $\frac{1}{D_e}$.

Thus the volume of the cell is $\frac{K}{4\pi D_e^2}$.

The energy-density is $\frac{2\pi D_e^2}{K} = \frac{B_e^2}{8\pi K} = \frac{KH_e^2}{8\pi}$.

The volume of an energy-cell is proportional to the square of its length measured along a line of force. Figs. 1 and 2 show how in general the portion of the line of force intercepted between two equipotential surfaces diminishes as the movement proceeds. The volume of the energy-cell constantly tends to diminish, though in some cases, as in fig. 2, the volume of some of the cells has to increase for a while to

Fig. 3.

Fig. 4.

allow the rest to contract. During this contraction the length of the cell bears to its area the constant ratio $\frac{K}{4\pi}$.

It has seemed worth while to trace roughly the curves of equal energy-density in the æther about equal unlike and equal like particles. These are shown in figs 3 and 4. The numbers apply to masses of 100 with a distance 10 between them.

7. Maxwell has discussed (Scientific Papers, vol. i. pp. 570–571) the modifications which must be made in the theory to make it fit in with the observed facts of gravitation.

The energy diagram for two gravitational particles is the same as that for two like electrified particles. The polarization tubes go off to infinity, and do not, as far as we know, end on negative gravitational matter.

The properties of the cells between the polarization tubes and the equipotential surfaces are exactly opposite in the two cases of electricity and gravitation.

The electrical energy-cells are constantly tending to contract both in length and section, but so that the area of the section always bears a constant ratio to the length of the cell. The gravitational energy-cells, on the other hand, constantly tend to expand, the same ratio holding between area and length as in the former case. While each electrical cell contains according to Maxwell's theory half a unit of energy, the gravitational cells must be supposed to contain half a unit less of energy than the same volume of undisturbed æther. The gravitational cells are negative energy-cells. This expansion of the negative energy-cells implies a kind of contraction of the energy of the gravitational æther. In the case of electricity the final state is reached when the energy-density is everywhere zero, all the energy having passed into the particles; in the case of gravitation when the density is uniform over a series of concentric shells, being a maximum at an infinite distance from ponderable matter.

8. Fig. 2 shows the path of the negative energy-cells, when two equal gravitational particles come together from an infinite distance apart. It can be seen that the cells retreat from the particles as these approach one another. There will be a greater number of negative cells in the æther when the par-

ticles are in contact than when they are at a distance. This is merely another way of saying that (positive) energy has passed from the æther into the particles.

The instantaneous position of the lines of energy-flow, for a given position of the moving gravitational particles, is something like fig. 2, the motion being away from the median plane and towards the line joining the two particles. The flow of energy is on the whole in the direction opposite to the motion of the particle. The potential energy absorbed by two gravitational particles, when they fall together, comes from the space between them.

The increase in the number of negative energy-cells, when two gravitating masses approach, is equal to twice the gain in kinetic, or loss in potential energy. The proof is the same as in the case of static electricity, due regard being paid to the signs of the quantities involved.

Thus the theory may be advanced that each of these negative energy-cells contains half a unit less of energy than the same volume of æther in which no such cells exist. An increase in number of these cells corresponds to a flow of energy from the gravitational æther into matter, where it is converted into kinetic energy.

Some difficulty may arise in special cases on account of the fact that in the case of gravitation the attracting mass has a volume distribution, instead of being confined to a surface like static electricity on a conductor. Each unit mass sends out a tube of polarization, whether it is on the surface or not, and a considerable proportion of the energy-cells exist inside the surface.

In the case of a single homogeneous sphere, at a distance from all other bodies, one sixth of the negative energy-cells are within the surface.

It is clear, then, that in general the energy is not removed from the æther at the instant the negative cell passes out through the surface, but perhaps rather at the instant that it comes out from the molecule. In other words, energy may be regarded as flowing in through the surface, but is only absorbed and converted into kinetic energy when it passes into a molecule.

9. Maxwell has calculated the enormous pressure along the

lines of force and the equal tension at right angles to them required, according to his theory, to account for the attraction of the earth by the sun. A minimum value for the amount of energy in one cubic centimetre of gravitational æther can be calculated by finding the negative energy-density on the surface of the sun considered as a body of uniform density.

The volume of the energy-cells at any point is $\frac{4\pi}{H_e^2}$.

The intensity of the gravitational field on the surface of the sun is $H_e = \frac{M}{r^2}$, where M is the mass and $r$ the radius of this body. If $\rho$ is the density of the sun the volume of an energy-cell is

$$\frac{4\pi r^4}{M^2} = \frac{4\pi r^4}{(\frac{4}{3}\pi\rho r^3)^2} = \frac{9}{4\pi\rho^2 r^2}.$$

The amount of energy lacking in each of these cells is half a unit. Hence one cubic centimetre of æther lacks $\frac{2}{9}\pi\rho^2 r^2$ units. These are static units of energy. One dyne equals $1{\cdot}544 \times 10^7$ static units of force, therefore one erg equals $1{\cdot}544 \times 10^7$ static units of energy. Take $r$ as $6370000 \times 100 \times 110$ centim. and $\rho$ as $1{\cdot}39$. Then the density of negative energy at the surface of the sun will be

$$\frac{2}{9}\,\frac{\pi \times 1{\cdot}39^2 \times 637^2 \times 110^2 \times 10^{12}}{1{\cdot}544 \times 10^7} \text{ ergs per c.c.}$$

$$= 4{\cdot}289 \times 10^{14} \text{ ergs per c.c.}$$
$$= 42{\cdot}89 \times 10^6 \text{ joules per c.c.}$$
$$= 16 \text{ horse-power hours per c.c.}$$

This would seem to mean that, at a distance from all gravitating matter, a cubic centimetre of æther contains at least this amount of energy.

10. That the theory may require an even greater energy-density than this is seen as follows. Suppose the energy of the gravitational æther to be due to vortex filaments or tubes of directed energy interlacing in every direction. Take at any point three axes at right angles to one another. The irregular distribution can be replaced in imagination by six equal sets of filaments parallel to the positive and negative directions of these three axes.

In space at a great distance from gravitational matter each of these sets of filaments will contain the same amount of energy. Let $6a$ be the amount of energy in one cubic centimetre of free æther. Let the positive direction of the X-axis at a point correspond with the positive direction of the gravitational line of force at that point. Let $b$ be the volume of the gravitational energy-cell. Then five sets of filaments in the cell may contain $5ab$ units of energy, and the sixth, which has the direction of the X-axis, $ab-1$ units. Altogether the cell will contain $6ab-1$ units, while the same volume at a distance from gravitational matter will contain $6ab$ units of energy.

This would require the existence of 96 or say 100 horse-power hours in every cubic centimetre.

11. It is an interesting question whether this theory of energy-distribution in gravitational æther is or is not the simplest and most probable. That other distributions are conceivable appears evident. For example, the æther along the straight line joining the centres of two bodies might be regarded as a stretched elastic cord, the laws of contraction being of course quite different from those which hold for ordinary elastic bodies.

Another explanation which seems possible in the case of two gravitational particles is as follows. In the energy diagram for two equal electrified particles with opposite sign, suppose each infinitesimal tube of polarization to be divided into two equal tubes with opposite directions. If they are regarded as vortex filaments, each vortex will work in with its neighbours rotating the other way, like one friction-pulley on another.

Then it is clear that there is no way in which we can regard the two particles as opposed in sign, and yet if each of the two sets of vortex filaments acts as electrostatic tubes always act, the particles will be attracted together.

The energy-flow in this case will be as indicated in fig. 1, and the distribution of energy-density as in fig. 3. It has not been found possible to map the energy field in this manner for three or more particles. Indeed, the difficulties are such that it seems improbable that this method can be applied.

12. In conclusion it may be well to notice again the

assumption on which this paper is based : that the energy-cells preserve their identity, and carry the same energy with them throughout their path. It is not clear that this is necessarily true. It may be that energy passes from the potential into the kinetic form in the æther itself, and not merely on the surface of the molecules. Kinetic energy may consist of the motion of the whole system of energy-cells. This would lead us very near the theory which regards the molecule as being nothing but the mathematical centre from which forces proceed, or perhaps, from another point of view, as having infinite extension.

## XXXV. *On a Simple Form of Harmonic Analyser.* By GEORGE UDNY YULE, *Demonstrator in Applied Mathematics, University College, London*[*].

> "The subject of the decomposition of an arbitrary function into the sum of functions of special types has many fascinations. No student of mathematical physics, if he possess any soul at all, can fail to recognize the poetry that pervades this branch of mathematics."—OLIVER HEAVISIDE.

§ 1. ABOUT a year ago several instruments for determining the coefficients of a Fourier Series expressing the equation to a given curve were described before this Society by Professor Henrici[†]. One of them, Professor Henrici's shifting-table analyser, used a planimeter as the integrator; an arrangement that seemed to me very noteworthy from the point of view of simplicity and cheapness. The analyser I am going to describe also uses a planimeter: consequently it can also only give the value of one coefficient at a time.

§ 2. Let P Q R be the curve to be analysed. Let the base P R range from $x=-l$ to $x=+l$, and the equation to the curve in terms of a Fourier Series be

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[*] Read March 8, 1895.

[†] *Ante*, p. 77; also Catalogue of the Mathematical Exhibition at Munich (1892-93).

$$y = \tfrac{1}{2}A_0 + A_1 \cos\theta + A_2 \cos 2\theta + \ldots$$
$$+ B_1 \sin\theta + B_2 \sin 2\theta + \ldots,$$

where

$$\theta = \pi x/l$$

and $\frac{1}{2}A_0$ is the mean ordinate of the curve. The values of the other coefficients are given by

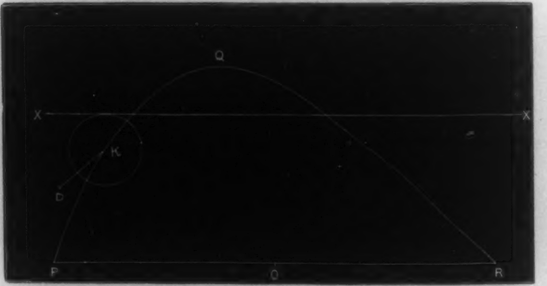
$$A_n = \frac{1}{l}\int_{-l}^{+l} y \cos n\theta \, d\theta,$$

$$B_n = \frac{1}{l}\int_{-l}^{+l} y \sin n\theta \, d\theta.$$

These are the integrals which any harmonic analyser has to evaluate.

Now suppose we have a circular disk, centre K (fig. 1), constrained to keep in contact with a straight line X X parallel to P R, and capable of rolling along X X without slip. Further, let X X be capable of motion in the plane in a vertical but not a horizontal direction, so that every point fixed in it describes a perpendicular to P R. Then we can make the point K trace out any arbitrary curve by moving X X and rolling the disk along it.

Fig. 1.



Bring K over P, and then mark any point D on the horizontal diameter at a distance $r$ from the centre (not necessarily inside the disk). Starting from P carry K right round P Q R and back to P again by the motion just described. Supposing the circumference of the disk to be an aliquot part of P R, say $2l/n$, let us find the area of the curve traced out by D during this operation. As the disk turns through an angle $2n\pi$ in rolling along a length $2l$ of X X, it will turn through $n\pi x/l$ in a distance $x$; so if $x, y$ be the coordinates of K at some point on its journey, the corresponding coordinates of D will be

$$x - r \,.\, \cos n\pi \,.\, \cos n\theta,$$
$$y + r \,.\, \cos n\pi \,.\, \sin n\theta,$$

where, to fix the sign, we have assumed D to lie initially to the left of K and X X to lie above the disk, as in the figure.

Hence the area traced out by D is

$$R_1 = \int y\,dx - r \,.\, \cos n\pi \int y\, d\,(\cos n\theta)$$
$$+ r \,.\, \cos n\pi \int \sin n\theta\, dx - r^2 \int \sin n\theta\, d\,(\cos n\theta).$$

The last two integrals vanish on taking them round a closed curve. Nothing is added to either of the first two by continuing the integration from R back to P, as $y$ is then zero. Therefore, calling the area of the whole curve P Q R $\alpha$, we have

$$R_1 = \alpha + \cos n\pi \,.\, \frac{rn\pi}{l} \int_{-l}^{+l} y \sin n\theta \,.\, dx.$$

Similarly, if D had been initially on the vertical instead of on the horizontal diameter, and below K, we should have had

$$R_2 = \alpha + \cos n\pi \,.\, \frac{rn\pi}{l} \int_{-l}^{+l} y \cos n\theta \,.\, dx.$$

It will evidently be convenient to take $r$ some multiple of $1/\pi$ units of length, say 10. We then have, rewriting the last two equations,

when $r = 10/\pi$

$$R_1 = \alpha + \cos n\pi \,.\, 10nB_n, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$R_2 = \alpha + \cos n\pi \,.\, 10nA_n. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Care must be taken with regard to the sign on the right-hand side if any other initial position of disk and line be assumed than that dealt with above.

§ 3. These two equations contain the whole theory of my instrument; they show how to construct a curve the area of which gives the required coefficients. The geometrical mechanism seems to me to be somewhat interesting, and to be possibly capable of generalization by the use of noncircular disks.

The area of the D-curve (in dealing with a material instrument) might be obtained in two ways. We might put a pencil through the disk at D, draw the curve, and integrate it afterwards: or we might attach the pointer of an integrator to D and let the integrating go on simultaneously with the following of the curve.

It is the latter alternative that I have adopted. The former method would have some advantages, but would be slow and would lead to mechanical difficulties.

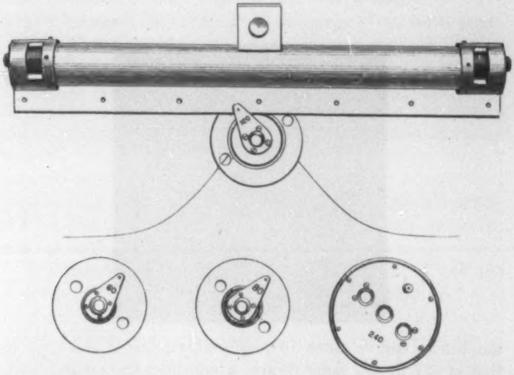
§ 4. The first analyser on this principle was made for me last summer by Mr. James Hicks. Though suffering from sundry defects (due entirely to my own design) it proved a really useful and workable analyser, but required too much care and patience in use. The construction has now been entirely revised. The present instrument, designed by Mr. Horace Darwin and made by the Cambridge Scientific Instrument Company, is the final outcome. For several suggestions I am indebted to Professor Karl Pearson.

The ruler XX of fig. 1 is a rolling parallel ruler with a rack cut along its front edge (fig. 2). The weight of the rack is counterbalanced by a block projecting from the back of the rule. Normally this block swings just clear of the paper, but it may be held down when one wants to keep the ruler still.

Corresponding to the disk of fig. 1 we have a series of toothed wheels; the number of teeth in the successive sizes being 240, 120, 80, and so on. Four of these disks have actually been made; they would probably be workable up to the sixth. The analyser is intended to work to a base-length of 30 centim.; the rack being cut 8 teeth to a centimetre. The ruler itself is made longer for the sake of stability.

The largest disk is the simplest. It is a flat disk of brass with teeth cut round the edge. Three windows are cut through it. One, in the centre, is glazed, and the centre of the glass is marked (on the side next the paper) with a black dot, the "tracing dot." The two remaining windows are provided with reference marks that give with the centre dot a base-line for setting the disk in any desired position. A small conical hole is made in the top of the disk, on a radius perpendicular to its base-line at a distance $10/\pi$ centimetres from the centre. This hole serves to receive the tracing-point of an ordinary Amsler planimeter, which performs the integration. The smaller disks are built up in three layers—a flat bottom plate, the toothed wheel, and a projecting crank, in the top of which is the planimeter hole. This hole is outside the circumference of the toothed wheel, so a crank or some such device is necessary. The crank swings clear above the rack when the wheel is in gear. The windows are arranged as in the first disk.

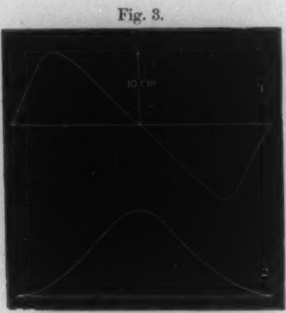
Fig. 2.



§ 5. The ordinary pattern Amsler planimeter with an arm about 16 centim. long does very well, but the tracer must be made vertically adjustable. The alteration is easily made without risk of damage. The planimeter remains of course available for its ordinary purposes, and for the determination of the absolute term.

The travel of the ruler is limited in two ways: first by the "reach" of the planimeter, secondly by the risk of running the reading wheel into the rack. Curves to be analysed must consequently be drawn to a moderate scale, but the permissible magnitude varies with the type of curve. If the type be anything like (1) of fig. 3 (sine type), 10 centim. amplitudes can be taken in comfortably; but if the type be that of (2) in the same figure, a considerably smaller scale must be used. In cases of physical curves (*e.g.* E.M.F. curves of alternators, conduction-of-heat curves) one is generally free to choose the limits of the period so as to bring the curve to the desired type.

Fig. 3.



The accuracy of the instrument will be measured by the accuracy of the planimeter. This cannot be fairly stated in percentages, as an error of unity in the vernier reading is never difficult, and may be anything per cent. in a small total. I strongly recommend drawing curves on cardboard; it is much more favourable to the planimeter than drawing-paper. The following tests may be taken as typical of the results that are obtained with care: the curves were drawn on card:—

(1) Actual curve,

$$3{\cdot}13 + 4{\cdot}60 \cos\theta + 1{\cdot}82 \cos 2\theta + {\cdot}39 \cos 3\theta + {\cdot}045 \cos 4\theta.$$

Analyser,

$$3{\cdot}14 + 4{\cdot}58 \cos\theta + 1{\cdot}84 \cos 2\theta + {\cdot}39 \cos 3\theta + {\cdot}042 \cos 4\theta.$$

(2) Actual curve (sloping straight line),

$$6{\cdot}37 \sin\theta - 3{\cdot}18 \sin 2\theta + 2{\cdot}12 \sin 3\theta - 1{\cdot}59 \sin 4\theta.$$

Analyser,

$$6{\cdot}39 \sin\theta - 3{\cdot}20 \sin 2\theta + 2{\cdot}11 \sin 3\theta - 1{\cdot}58 \sin 4\theta.$$

The units are centimetres.

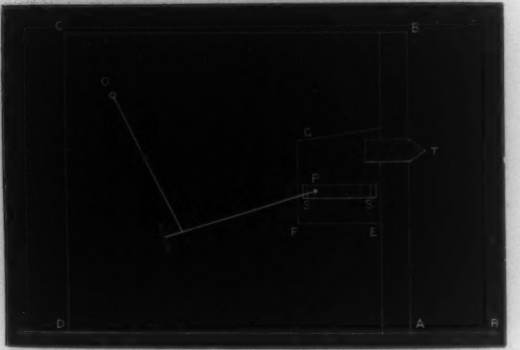
§ 6. So much for the accuracy and range of the instrument. To get any desired coefficient, the ruler is set with its edge parallel to the curve-base and with the proper disk in gear. Ruler and disk are then adjusted till the tracing-dot stands over the point P (fig. 1), and the base-line of the disk is either vertical or horizontal according as a sine or cosine term is wanted. The planimeter-point is finally dropped into the hole provided for it, and the tracing-dot carried completely round the curve. The resulting planimeter reading will be the area of the curve plus or minus $10n$ times the desired coefficient.

Both hands must be used in guiding the disk, as rack and disk have to be held together while the latter is turned. The operator forms, in fact, an essential link of our mechanism which without him is unconstrained. It is this liberal use of the operator that enables me to dispense with slides, carriages, and other expensive things, and thus gain in simplicity.

§ 7. This analyser arose from a simple form of step-by-step integrator or "adder" which may be worth a brief description. The instrument is shown diagrammatically in fig. 4: it was made from materials at hand and I describe it as made. A B C D is a square sheet of card with a foot-rule glued along one edge A B. A set square F E G can be slid up and down along this rule: it is provided with a tracer T and some scales of sines S S. The whole sheet of card is guided parallel to the axis of $x$ by a T-square D A R clamped to the drawing-board: if the card is pulled forward by the corner A the friction keeps it set against the square. O P is a planimeter with its pole fixed to the card and its pointer P resting on one of the scales of sines, which must stand parallel to the axis of $x$.

Mark off along the base of the curve to be analysed a number of equal divisions, *e. g.* 6° each, and erect the ordinates $y_1, y_2$, &c. at the centres of each of these elements. Suppose the pointer P of the planimeter to rest initially at the zero of the scale, and the tracer T attached to the set square to stand over the origin of the curve. Pull the card forward, carry T to the top of $y_1$, and then shift P to 6° on the scale. Pull the card forward again, carry T to the top of $y_2$, and then shift P to 12°. Continue this procedure right on to the end of the curve.

Fig. 4.



P will then have come back to its starting-point on the scale, after describing on the card a certain curve or stepped polygon. The area of the polygon is

$$\begin{aligned} & y_1 (\sin 6^\circ - \sin 0^\circ), \\ & + y_2 (\sin 12^\circ - \sin 6^\circ). \\ & + y_3 (\sin 18^\circ - \sin 12^\circ), \\ & + \quad . \quad . \quad . \quad . \quad . \quad . \quad . \\ & + y_4 (\sin 360^\circ - \sin 354^\circ), \end{aligned}$$

a quantity which (as the elements are small) approximates to

$$\int_0^{2\pi} y \, d(\sin \theta).$$

Thus the planimeter-reading after this procedure gives us the first cosine coefficient. I need not enter at length into the mode of getting the others. For the second coefficient one would have to shift the tracer P 12° at a time instead of 6°, and so on.

In my case I actually used steps of 6°, as above; and there were three scales on E F G going by steps of 6°, 12°, and 18° respectively for the first three terms, the separation of the scales helping to avoid confusion. The results were good: for example, in one test the actual coefficients were 4·82, 1·09, ·009: the instrument gave 4·86, 1·08, ·01. The chief objection to such a non-automatic integrator is of course that one is liable to forget to shift the planimeter pointer at some stage of the proceedings. The chief advantage is that your curve need not be drawn to any particular base-length. Whatever the base, it is only necessary to divide it into the proper number of equal parts, and erect the ordinates at the centres of these elements.

Suppose we wished to make the arrangement automatic. We might substitute for the harmonic motion of P along S S a circular motion round the centre of S S. This merely amounts to giving P another harmonic motion (perpendicular to S S), a proceeding which adds nothing to the planimeter-reading if the integration be continued completely round the curve.

But this is not an easy motion to obtain mechanically. The difficulty is obviated at once if we remove the card A B C D altogether and fix the pole of the planimeter in the drawing-board. If we give P the same circular motion as before we have the "disk" analyser, which I described in the first part of this paper. The area of the curve analysed is added to the integral given by the planimeter, but that is all.

Evidently in the instrument of fig. 4 we have only taken a special case in making the scales scales of sines. We might have used scales graduated proportionally to $x^n$ and got moments. Any other integral could be obtained approximately if a proper scale could be drawn.

## DISCUSSION.

Prof. HENRICI said he had at one time considered the question of constructing an analyser which should employ a planimeter as the integrator, and he was particularly pleased with the instruments exhibited. Since the area required was the difference between the area of the original curve which is traced out by the centre of the disk (K) and the curve traced out by the point D, and since this area is really the area swept out by the straight line KD, if we attach an integrating wheel to the disk with its axle parallel to KD, the required area can be directly obtained from the reading on this wheel. In addition, if a second integrating wheel were fixed to the disk with its axle perpendicular to KD, the coefficients of $\cos n\theta$ and $\sin n\theta$ could be both obtained by going round the curve once. The instrument devised by Mr. Yule was practically the inverse of one he (Prof. Henrici) had invented.

Dr. Burton pointed out some incorrect signs in the proof given. These, however, do not affect the final expressions obtained.

Mr. Inwards suggested that errors due to back-lash might be avoided by using either a double wheel or a double rack, so that by means of a spring each side of the teeth which were engaged might be in contact at the same time.

## XXXVI. *On the Objective Reality of Combination Tones. By* A. W. Rücker, *M.A., F.R.S., and* E. Edser, *A.R.C.S.*[*]

The question of the objective existence of combination-tones has been keenly disputed. At first they were regarded as produced within the ear itself. Von Helmholtz in part adopted this view, and gave a theoretical explanation of the way in which the construction of the ear might lend itself to such a result. ('Sensations of Tone,' App. XII.) He also believed that they existed objectively when the amplitudes of the vibrations of the notes which give rise to them are so great that powers higher than the first have to be considered. He supported this view by mathematical demonstrations, and stated ('Sensations of Tone,' transl. by A. Ellis, p. 157) that he had proved their objective existence by making membranes and resonators to respond to combinational tones produced by the siren and harmonium. These views and statements have been adversely criticised by König, Bosanquet, and Preyer. A very lucid account of the controversy was given by the late Mr. Ellis in his translation of the *Tonempfindungen*, and the net result of the impression produced in his mind is shown by two notes on pages 156 and 157. He there states that the result of Mr. Bosanquet's and Prof. Preyer's experiments is to show that the combinational tones are produced in the ear itself, and that it is probable that the apparent reinforcement of the resonators noticed by Helmholtz arose from imperfect blocking of both ears when using them.

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[*] Read March 22, 1895.

These statements were unqualified, and no condition was made as to the way in which the combination-tones were produced. Helmholtz, for reasons which we need not recount, regarded the siren as the best instrument for producing objective combination-tones ; and we recently determined to submit the question of their existence, which seemed to be decided against him, to another experimental test.

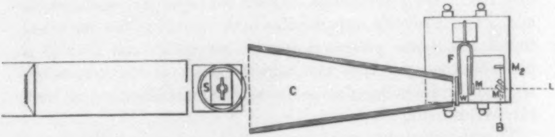
In this paper we give the result of our investigations, as far as they have at present been carried out. We do not regard them as complete, but they at all events prove that when the conditions under which we experimented are fulfilled, there can be no doubt that difference- and summation-tones are produced which are capable of disturbing resonating bodies.

The resonator employed in the first instance was a tuning-fork. It is well known that this instrument is relatively difficult to excite by resonance, and it was therefore necessary to use an extremely delicate method of detecting whether it was set in motion. For this purpose a mirror attached to one of the prongs was made one of a system by which Michelson's interference-bands were produced. A movement of the prong amounting to half a wave-length of light (say 1/80,000 of an inch) would alter the length of the path of one of the interfering rays by a wave-length. A periodic vibration of this amplitude would cause the band to disappear.

It is therefore evident that an extremely minute movement could be detected. It was at first open to question whether the apparatus would not be so sensitive to accidental disturbances as to be untrustworthy. This difficulty has, however, been entirely overcome.

A plan of the apparatus is shown in fig. 1. The shank of the tuning-fork, F, is imbedded in a mass of lead. One of the prongs carries a mirror, M. To the other is attached a square of wood, W, of larger area but of the same weight as the mirror. A Lissajous' figure (an ellipse) was formed by reflexion from the mirror and from a small square of silvered glass attached to one of König's large forks adjusted to give the C of 64 complete vibrations per second, and the pitch of F was adjusted until only one beat occurred in two minutes. The pitch was thus very accurately known. A double siren, S, was placed between a large König resonator tuned to 64 vibrations and a wooden cone or pyramid, C. The end of the cone was placed about half an inch from W, which was rather larger than the narrow end of the cone. The sensitiveness of the apparatus depended in part upon the distance between W and C. If the distance was too large, the sensitiveness was diminished. If it was too small, the instrument was unduly affected by chance puffs of air even when not periodic in character.

Fig. 1.



A source of light, L, was used to form a system of interference-bands by means of the half-silvered mirror $M_1$, and the two mirrors M and $M_2$. The two interfering rays travelled over the paths $LM_1M_2M_1B$ and $LM_1MM_1B$ respectively. The distances $MM_1$ and $M_1M_2$ were approximately equal; and since when soda-light was used a change in the length of either of the paths of $\frac{1}{2} \times 589\,\mu\mu$ would cause a dark band to shift into the position previously occupied by the next bright band, and since, further, any movement of M altered the length of the path of the ray by twice its own magnitude, it is evident that a movement of $\frac{1}{2} \times 589\ \mu\mu$, or, say, of one hundred thousandth of an inch, could be easily detected.

The fork F and the mirrors M, $M_1$, and $M_2$ rested on a square stone, which was suspended by wires and india-rubber door-fasteners from a heavily weighted beam, which itself rested on india-rubber balls placed at a convenient height on a double pair of wooden "steps." With these precautions it was found that the bands remained tolerably steady even by day when persons were moving about the building, and when the traffic on the frost-bound road produced considerable mechanical vibrations. Even under these conditions, we have satisfied all who have seen the apparatus of the reality of the phenomena. The experiments on which we rely, however, were made on several occasions between midnight and 2 or 3 A.M. The bands were then absolutely clear and steady. They were undisturbed for many minutes at a time when the bellows were being worked and the siren was sounding loudly. It was only when a note of 64 vibrations per second was directly or indirectly produced that they vanished, and there could be no possible doubt or mistake as to whether the disturbance was or was not produced by the sound or combination of sounds under investigation.

Up to the present we have used the fork above described only. It was chosen because it was fairly stiff, and as removable metal mirrors for the production of Lissajous' figures were attached to its prongs, it was possible to replace them by the glass mirror and square of wood without altering its pitch. It would be quite possible to use properly made forks of higher pitch as resonators, and the steadiness of the bands at night is so remarkable, that we believe that if the apparatus were set up in the country, on a stone isolated from the rest of the room, the degree of sensitiveness we have attained could be far surpassed.

### *Tuning the Siren.*

Three methods were used for determining when the siren was producing the required notes. When one of these was fairly high, the beats given by it and a standard fork were noticed, and the note could thus be kept hovering about the required pitch for a considerable time. Although with the aid of König's large forks we could apply this method to vibration-frequencies of 48 per second and upwards, it was difficult when the notes were very low to recognize the beats with sufficient certainty.

The prongs of various tuning-forks were therefore furnished with two pieces of tin-foil, which opened and closed a slit made in them twice in every complete vibration. They were also compared with a standard by the aid of a revolving cylinder, and were adjusted by weights to the required frequencies. These were so selected as to make one of the circles of holes on the siren appear stationary when viewed through the slit, if the velocity of rotation was such that the desired note or notes would be given by the same or other circles of holes. An observer watching the siren through the slit and pressing lightly on the axis with a straw, was able to adjust its speed so that the required combination of sounds was produced for several, and in some cases for many seconds at a time.

We have also projected the image of the row of holes on a screen, the cone of light passing at its narrowest part through the slit in the tinfoil screens carried by the auxiliary fork. When the upper siren was to be used, two semicircles of light mirror-glass were laid on the disk of the lower siren to which the two halves of a paper cog-wheel were fastened. The image of the cogs could thus be projected.

The third method of determining the speed of the siren depended on the use of an instrument first devised by Lord Rayleigh in 1880. A mass of air enclosed in a tube is excited by resonance, and the fact of the excitation is indicated by a light mirror set where the motion is greatest, and inclined at 45° to the direction of the air-currents. In accordance with the general law that a lamina tends to place itself perpendicular to the direction of a stream, the mirror moves when the air vibrates. In the original apparatus the amount of the movement was controlled by magnets. Since that date Professor Boys has modified the instrument by substituting a quartz-thread suspension for a silk fibre, and using the torsion of the thread instead of the directing force of the magnets. He exhibited the apparatus during a lecture delivered before the British Association in Leeds. It may be called a mirror-resonator.

Professor Boys has been good enough to make two of these instruments for us, and it was decided that one of them should respond to 161 vibrations per second. The movement of the spot of light reflected from the mirror informed us when the siren was giving this note, and this fact was utilized in one of the experiments.

### *Sensitiveness of the Apparatus.*

The results were in general improved by laying a small strip of dry blotting-paper upon the prongs. Mere accidental disturbances died out more quickly, and the vibrations of the fork diminished more rapidly, when the notes which had produced them ceased to sound.

A forced movement could be produced in the fork by blowing directly down the collecting cone, but a small organ-pipe could be sounded, or a König's fork bowed near the opening without producing the least effect if the frequency of the note produced was not near 64 per second. In like manner many notes of two reed wind-instruments, somewhat similar in construction to the harmonium, were sounded simultaneously so that the room echoed with discordant sound, yet without producing the least effect on the steadiness of the bands.

On the other hand, when one of König's forks tuned to 64 vibrations was touched with the india-rubber covered handle of a gimlet, or was struck with a piece of gas-tubing so lightly that an observer with his ear close to the fork could not detect the fundamental note, the bands instantly disappeared.

It was therefore evident that the apparatus could respond to a vibration which was quite inaudible to a person standing by the resonating fork.

When the König fork was weighted so as to give 63·5 vibrations per second, the bands appeared and disappeared at regular intervals of two seconds, thus corresponding to the beats between the exciting and resonating forks. The bands were not disturbed when the beats exceeded 2 or 3 per second unless the exciting fork was bowed very violently. In the experiments with fainter tones, the resonating fork was only disturbed when the frequency of the exciting note agreed very exactly with its own.

As the speed of the siren was gradually increased from rest the bands always disappeared two or three times, the disturbance being no doubt caused by the upper partials as the vibration-frequency passed, in turn, the values 16, 21·3, and 32 per second. No exact measurement was made of the corresponding frequencies, as there could be no question as to whether the partials were produced or as to whether the apparatus could detect them. No such disappearance occurred when the note was higher than C, except in the case of certain spurious effects referred to below.

All the experiments were performed several times on each occasion, and on two occasions at least. The bands were sometimes produced by soda-light, and watched by an observer through a telescope.

Sometimes the electric light was used. The bands could then be projected on a screen side by side with the image of the holes or cogs. In this way information as to the note produced and as to the behaviour of the bands was simultaneously conveyed to all who watched the experiments.

## *Precautions.*

It will not be thought remarkable that so delicate an apparatus requires careful use.

In the first place, it was necessary to be sure that the disturbance ascribed to the joint action of two notes was not produced by one or both of them when acting alone. In all cases, therefore, in which it was possible to determine the pitch of both notes separately, each note was sounded alone and carried slowly past the particular pitch at which the existence of a combination-tone was to be investigated. In general, no effect was produced; but after the apparatus had been in use for some little time, we were troubled by the fact that two notes which did not differ much from 256 and 320 vibrations respectively disturbed the bands when they were produced separately.

That these effects were spurious was evident from two facts. Firstly, the same notes had previously been sounded for a long time with the special object of determining whether they produced any effect, and had produced none. Secondly, the disturbances were evidently forced. When the fork has been disturbed by a vibration of frequency 64, it continues to oscillate for several seconds after the disturbing note has ceased. The bands alternately appear and disappear several times before the final state of rest is attained. In the case of a "spurious" effect, the bands reappear instantaneously with absolute clearness the moment the disturbing note ceases, thereby indicating a forced vibration. It was, however, a more difficult task to discover the cause than to determine the character of these disturbances. Finally, it was found that since the apparatus was first set up some cracks had opened in the wooden pyramidal collector. A tap on the side of this will disturb the bands; and when one of the cracked sides was loaded with weights the disturbance due to the 320 note was much reduced. The cracks were then cut out, the defects made good; and since that time this disturbance has entirely ceased.

The effect produced by the 256 note was due to another cause. When the pyramid was removed, the open ends of the resonance-boxes of various tuning-forks (256, 320, 384) were held near the square of wood which was attached to the fork F. It was found that the 256 fork was the only one which affected the bands, and that it only produced any result when the sounding-box was held near that part of the wood which projected beyond the end of the prong. It was therefore evident that the two ribs attached to this were not sufficient to prevent a certain flapping of the projecting part, and that this responded to a note of about 256 vibrations. The end of the collecting pyramid was then shifted a little so that the waves of sound impinged only on the more rigid part of the wooden square, and the spurious effect immediately and completely disappeared.

Of the notes which caused these troubles, the lower one was decidedly lower than the *c′* of 256; the other corresponded very accurately with the *e′* of 320. The fact that both these numbers are multiples of 64 may legitimately give rise to the doubt whether the fork F can be set in motion by disturbances which are multiples of its own frequency.

Even if it be admitted that such forced vibrations would be especially easy to produce, we must insist—(1) that we can distinguish (as above described) between forced and natural vibrations; (2) that when the apparatus was properly arranged such notes could be produced by the siren for long intervals of time without the least effect on the bands; (3) that two tuning-forks, of 256 and 320 vibrations respectively, have been placed within the wooden pyramid with their sounding-boxes resting on and supported by, the lower side, yet no effect was produced on the bands even when they were both sounding loudly at the same time; (4) that one of König's large forks, with a frequency of 128, was placed in front of the collecting cone and produced no effect when sounding loudly, though the slightest tap on the 64 fork caused the bands to vanish for many seconds; (5) that the 320 and 384 forks produced no effect when the pyramid was removed and they were held as above described close to the receiving prong of the fork; (6) and, lastly, that in two out of the five experiments on the difference-tones, and in all those in which the interference apparatus was used to detect summation tones, the frequencies of the notes employed were neither multiples nor sub-multiples of 64.

As in all the above experiments the resonator was in position, they also sufficed to prove that tones of 64 vibrations were not manufactured in it by the primary notes when acting singly.

If the objection is raised that, although neither note disturbed the bands when sounded alone, the effect might be due to the double disturbance produced by the two sounds, we think it sufficient to answer that we have always carried the two notes above the pitch at which the difference-tone might be expected to affect the instrument, then lowered the pitch again till the notes were too flat, and repeated this operation several times. The disturbances were only produced when the pitch was nearly, or very nearly, correct As soon as a few beats per second were heard the bands became visible.

Having thus described the various tests which were applied to the apparatus, we may proceed to describe the experiments without dwelling further on the necessary precautions. It is sufficient to say once for all that they were adopted in each case.

The main object of the enquiry was to obtain evidence as to the objective reality of the combination-tones, and for this purpose the following experiments were arranged.

Each box of the siren had four circles of holes which could be used separately or together. The number of openings in the upper box were 9, 12, 15, and 16, and in the lower 8, 10, 12, and 18. It will be convenient to refer to these as the 9 row of holes, and so on.

### *Experiment* I.

The 12 and 15 rows of holes in the upper box were opened, and the pitch was raised until the upper note gave slow beats with a fork of 320 vibrations per second. The lower note was then the C of 256 vibrations. The difference or beat tone of 64 vibrations affected the instrument powerfully. The experiment was tried both by night and by day. It was difficult to keep the siren exactly at the true pitch, but when the beats were very slow the bands continually disappeared, sometimes for many seconds at a time, then appeared for a moment and then disappeared again. As soon as the pitch was lost by a few beats per second, the bands remained steady and clearly visible.

The experiment was repeated with the 9 and 12 rows of holes. When the upper note was C of 256 vibrations, the lower note was 192 vibrations. The difference-tone of 64 vibrations affected the fork very powerfully.

The experiment was also modified by opening the 10 and 12 rows of holes. When the notes corresponded to 320 and 384 vibrations respectively, the bands disappeared as before.

### *Experiment* II.

In experiment I. the frequencies of the difference-tone and of König's first lower beat-tone were identical. The experiment was therefore varied by using 8 and 18 rows of holes. The frequency of the difference-tone was thus proportional to 10, while that of König's lower beat-tone would be $18-2\times 8=2$. When the siren was revolving at the rate of

6·4 revolutions per second, the two notes corresponded to 51·2 and 115·2 vibrations per second, the difference-tone being 64.

The pitch was determined on different occasions by different methods. Firstly, by noting the beats between the higher note and a König's fork adjusted to 115·2 complete vibrations per second, and secondly, by watching the row of eight holes through a slit carried by a fork which gave 25·5 vibrations per second.

The effect was rather feebler than in the last experiment, but there was absolutely no doubt as to the objective reality of the difference-tone. The bands regularly disappeared when the required pitch was obtained, and reappeared when it was lost.

Again the 15 and 9 rows of holes were used. The difference-tone is thus proportional to 6, and König's beat-tone to $9\times 2-15=3$. When the rate of revolution was $10\cdot\dot{6}$ the two notes were 160 and 96 respectively. In this experiment the mirror-resonator which responds to 161 vibrations was employed to determine the rate of the siren. The bands and the spot of light were sometimes watched together: on another occasion one observer who could not see the bands raised his hand whenever the spot of light moved. The bands invariably disappeared at the instant that this signal was made.

## *Experiment* III.

The next experiment was directed to determine the objective reality of König's lower beat-tone when the interval was greater than an octave. The 8 and 18 rows of holes being kept open as before, the speed was increased until the lower note was that of 256 vibrations. The upper note was then 576, and König's lower beat-tone was of $576-2\times 256=64$ vibrations.

We lay less stress on negative than on positive results; but we tried for a long time on two occasions to get evidence of the objective character of the note, but entirely failed. The pitch was determined by the beats with a 256 fork.

### *Experiment* IV.

We next turn to observations on the summation-tone. The 8 and 10 rows of holes were opened, so that when the cover made 3·55 revolutions per second the summation-tone would be that of $18 \times 3\cdot\dot{5} = 64$ vibrations.

The pitch of the notes given by the siren was again determined in different ways on different occasions. The summation-tone being produced in the lower box, the 15 row in the upper box was also opened, thus producing a note of $15 \times 3\cdot\dot{5} = 53\cdot\dot{3}$ vibrations per second. The required speed was determined by making the beats vanish between this note and a König's fork tuned to give 53·3 vibrations. With this method it was difficult to keep the speed constant for a length of time sufficient to disturb the resonating fork appreciably. When the pitch was altered very slowly the bands disappeared just as the right note was reached, and did not disappear at any other time during the experiment.

On another occasion the 9 and 12 rows of holes were opened, so that the summation-tone of 64 vibrations would be given when the siren made 3·05 revolutions per second. The 18 row of holes was watched through a fork of 27·2 vibrations, so that 54·4 views would be obtained while a hole moved over $18 \times 3\cdot05 = 54\cdot9$ intervals. Hence the right pitch was obtained when the holes moved slowly forwards. The bands invariably disappeared when this state of things was attained.

On a third occasion the lower cover of the siren was covered with a thin piece of silvered glass as above described, carrying a concentric circle of black paper, the edge of which was divided into 18 equidistant cogs. An image of these was produced on a screen by a lens, and made intermittent by the 27-vibrations fork. The disturbance due to the summation-tone was again and again made evident when the images of the cogs appeared to be moving slowly. In the intervals the bands were beautifully steady.

The earlier of these experiments were performed before, and the later ones after, the apparatus had been taken down and set up again in another room. They left in the minds of those who saw them no shadow of doubt as to the objective reality of a note corresponding in frequency with the summation-tone.

We now turn to experiments intended to throw light on the cause of the production of this note.

### *Experiment* V.

It has been suggested that the summation-tone may be the difference-tone of partials. König (*Acoustique*, p. 127) remarks that it may occasion some surprise that the particular harmonics whose difference-tone corresponds to the summation-tone should be especially prominent; but he points out that in some cases the difference-tones of the lower harmonics correspond either to the fundamentals or to some of their upper partials. In the case of the fourth (3 : 4), however, König remarks that the 5th partials would give a difference-tone (5) which could be distinguished from the lower partials, and that the difference-tone of the 7th partials would give the summation-tone. Now we have already proved (Exp. IV.) that the summation-tone produced by two notes separated by the interval of a fourth (9 : 12) is objective; and if this is due to the difference-tone of the 7th partials, there seems to be no reason why the difference-tone of the 5th partials should not be objective also, and probably more intense.

We therefore increased the velocity of revolution to 4·27 per second, the 9 and 12 rows of holes being opened as before. The frequencies of the two notes were thus 38·43 and 51·24. The pitch was determined by keeping the 12 holes nearly stationary when viewed 51 times a second by aid of the 25·5 fork. The first difference-tone was 12·81, and the difference-tone of the 5th partials was 64·05. When the speed corresponding to this difference-tone was attained there were occasional flickers of the bands, so that it is possible that it has an objective existence. But, on the other hand, the effect was less than that produced by the summation-tone. The bands never disappeared for any considerable length of time, as they did when the fork responded to the summation-tone, and the experiment left no doubt in our minds that the greater effect was produced by the summation-tone.

### *Experiment* VI.

The same point was also investigated in another way. If the summation-tone of two notes of frequencies $p$ and $q$

corresponds to the difference-tone of the $n$th partial, we must have

$$(p+q) = n(p-q),$$

where $n$ is an integer. If, however, the 9 and 16 rows of holes were opened,

$$p+q=25, \quad p-q=7;$$

so that the summation-tone could not be produced by partials of the same order. The 10th partial of the higher note beating with the 15th of the lower note $(160-135=25)$ would indeed have the same frequency as the summation-tone, but it appears to us absurd to suppose that so improbable a combination should produce appreciable results. It is true that lower partials may give beat-tones near to the summation-tone. Thus $5\times16-6\times9=26$. But if we are to assume that any pair of partials can thus produce objective tones, the number of combinations will be so great that the fork ought to have been disturbed frequently when the note of the siren was being raised to the required pitch. As a matter of fact, when once the C of 64 vibrations was passed, so that all the partials were higher than the pitch of the resonating fork, no such disturbances were ever observed except when the difference- or summation-tone of the primaries was produced. Putting, therefore, all such fantastic combinations aside, the experiment may be regarded as a test whether the summation-tone can be produced when it cannot be due to two partials of the same order.

When the velocity of revolution was 2·56 per second, the 16 and 9 holes gave notes of 40·96 and 23·04 vibrations. The sum of these is 64. The 12 holes were viewed through a slit alternately closed and opened by a fork of 15 vibrations per second, and when the holes appeared to move slowly the summation-tone caused the bands to disappear.

In this experiment, however, the third partial of the lower note corresponds to 69·12 vibrations, and we thought it desirable to make sure that the disturbance attributed to the summation-tone was not in reality due to this partial. This was the more important, because the difference in the speeds of the siren when the summation-tone and the partial in question corresponded to 64 vibrations was very small.

Thus, when the speed was 2·56 revolutions per second each of the 12 holes would advance through 30·72 intervals in a second, and since the fork gave 30 views per second the holes would appear to move slowly forwards.

When the speed was 2·37 revolutions per second the third partial of the lower note (9 row of holes) would be $3 \times 9 \times 2 \cdot 37 = 64$, and each hole of the 12 rows would advance through 28·44 intervals—that is, would appear to recede through 1·56 intervals per second. Thus the partial would be most efficient in promoting disturbance when the holes appeared to go backward with moderate speed.

The question to be answered was whether these two disturbances could be confused with each other.

When care was taken to keep the pressure in the wind-chest the same whether one or both sets of holes were opened, the effect of the partial produced by the 9 set of holes could hardly be detected. The bands were shaken a little when the row of 12 holes appeared to move backwards, but they did not disappear; whereas they were completely wiped out by the summation-tone when the two notes were sounded.

When the pressure on the wind-chest was increased, the rate of revolution being nevertheless maintained constant by pressing lightly on the axle of the siren with a straw, the effect of the partial was more marked, but it was always produced when the holes appeared to move backwards.

On the other hand, when both notes were sounded together and when the pitch was gradually *reduced* to the desired point, the disturbance always began when the holes moved slowly forwards. If the pitch fell very slowly it was possible to note a reduction of the disturbance, followed by an increase when the holes appeared to move backwards.

We thus convinced ourselves that the effects of the two sources of disturbance could be distinguished, and that the supposed summation-tone was not due to the partial of the lower note.

### *Experiment* VII.

We have also succeeded in demonstrating the reality of the summation-tone with a mirror-resonator constructed by Professor Boys to respond to a vibration-frequency of 576.

The rows of 15 and 12 holes being opened, notes of 320 and 256 vibrations were produced. When they were sounded separately, the mirror moved slightly. When they were sounded together, the spot of light was driven off the scale when the upper note coincided with that of a 320-vibration fork, but immediately returned when this pitch was lost.

The experiment was varied by using the 16 and 12 rows, and also the 16 and 9 rows. The summation-tone corresponds to 576 vibrations when the upper note is of 329·15 and 360 vibrations in these two cases respectively. The 320-fork was used, and the disturbance occurred in the one case when the pitch of the note was nearly the same as before, and in the other when it was about a tone higher.

We attach great importance to this corroboration of our results by an instrument of a totally different construction from that first employed.

The attempt to obtain proof of the existence of a difference-tone by means of the mirror-resonator of 161 vibrations has not been successful. The instrument is much less affected by the note to which it responds than is that which answers to 576 vibrations, even when that note is produced directly by the siren. It is, therefore, perhaps not wonderful that it gives no reliable evidence of the existence of a difference-tone.

We now sum up the results we have obtained in two tables.

Instrument. Interference Resonator.

| Number of holes in siren. | Interval. | Frequencies. | | Combination-tone. | | König's Beat-tone. |
|---|---|---|---|---|---|---|
| 12 and 10 | Minor Third. | 384 | 320 | 64 | Difference-tone. | 64 |
| 15 „ 12 | Major Third. | 320 | 256 | 64 | | 64 |
| 16 „ 12 | Fourth. | 256 | 192 | 64 | | 64 |
| 15 „ 9 | Major sixth. | 160 | 96 | 64 | | 32 |
| 18 „ 8 | Octave and major tone. | 115·2 | 51·2 | 64 | | 12·8 |
| 10 and 8 | Major Third. | $35{\cdot}\dot{5}$ | $28{\cdot}\dot{4}$ | 64 | Summation-tone. | |
| 12 „ 9 | Fourth. | 36·57 | 27·43 | 64 | | |
| 16 „ 9 | Minor Seventh. | 40·96 | 23·04 | 64 | | |

Instrument. Mirror Resonator.

Summation-Tones.

| Number of holes in siren. | Interval. | Frequencies. | | Sum. |
|---|---|---|---|---|
| 15 and 12 | Major third. | 320 | 256 | 576 |
| 16 „ 12 | Fourth. | 329·15 | 246·85 | 576 |
| 16 „ 9 | Major sixth. | 360 | 216 | 576 |

### *Negative Results.*

We have tried several times to obtain indications of combination-tones when the primary notes were produced by tuning-forks. Two of König's large forks adjusted to 48 and 112 vibrations produced no effect when bowed simultaneously before the collector, and, as has been stated, smaller forks giving 256 and 320 vibrations have been placed inside the collector when sounding loudly. No effect whatever was produced, and there can be no doubt that if objective combination-tones are produced in such cases they are very much less intense than those generated by the siren.

Experiments have been made with reeds and with organ-pipes, but up to the present with uncertain results in the first case and negative results in the second. We hope to investigate these cases further.

We have made several attempts to detect combination-tones of higher orders, such as $2p+q$ and $2p-q$, but without success.

### *Conclusion.*

We may in conclusion refer to some of the suggestions which have been made to account for the combination-tones by theories other than those of Helmholtz.

König's suggestion that they are the beat-tones of upper partials has been discussed and shown to be inadequate to explain the facts of observation.

Again, it has been argued that the summation-tone is the beat-note between the second partial of the higher note (the octave) and the beat-tone of the two primaries. It follows as a matter of algebra that such an explanation must always be numerically correct, for $2a-(a-b)=a+b$, and our experiments throw no new light on the matter. It appears to us, however, that since propinquity between the sources of sound, causing a violent disturbance, is favourable to the production of combination-tones, while it is not necessary for the production of beats, the facts of experiment are in this case also in favour of von Helmholtz's views.

A still more subtle objection has been taken by Terquem (*Annales d'Ecole Normale*, 1870, p. 356). When two rows of holes are open in the siren, there may be occasions on which all the holes of both rows are opened simultaneously and others on which only one row is in action at one time. Terquem attempts to calculate the effects of irregularities such as these, but in the first place he specifically refrains from attacking the theory of Helmholtz ; secondly, he does not apply calculation to the siren of Helmholtz ; thirdly, he points out that the relatively large size of the holes in that instrument would reduce the effects he predicts ; and, lastly, he admits that his results require confirmation by experiment. Putting these points aside, however, his theory leads to the conclusion that the two notes which we have been regarding as fundamental are reinforced harmonics in a series of which the fundamental note corresponds to the greatest common measure of these frequencies. Both the summation and the difference tone must be included in such a series ; but Terquem's theory gives no reason why they should have such exceptional importance as experiment proves that they have. Lastly, as he expressly repudiates the idea that partials have an objective existence (*loc. cit.* p. 274), and includes the combination-tones in a series of partials, the experiments described by us must on this point be regarded as opposed to his views.

We think, then, that our experiments prove that von Helmholtz was correct in stating that the siren produces two objective notes the frequencies of which are respectively equal to the sum and difference of the frequencies of the fundamentals, and that our observations are also more or less opposed to the theories by which König, Appun, and Terquem have sought to account for the production of these notes.

We believe that the method we have devised is capable of greater sensitiveness. It can be extended by employing forks of different pitches, and it is quite possible that less massive forks may enable us to detect effects which have hitherto escaped us. We therefore refrain from any wide generalizations until a wider foundation of experiment has been laid.

P.S.—Since the above was written Prof. S. P. Thompson has drawn our attention to a paper by O. Lummer, published in 1886 (*Verh. phys. Gesell. Berlin*, 1886, No. 9, p. 66), which had escaped our notice, as it is not abstracted in the *Beiblätter*. Herr Lummer obtained evidence of the objective character of the summation-tone by means of the microphone.

## XXXVII. *Some Acoustical Experiments. By* CHARLES V. BURTON, *D.Sc., Demonstrator in Physics, University College, London*[*].

### I. *Subjective Lowering of Pitch.*

1. A YEAR or two ago, in the physical laboratory of Bedford College, London, the professor, Mr. Womack, called my attention to the fact that a tuning-fork which was being used by a student appeared to rise perceptibly in pitch as the vibration died away. It then occurred to me that the effect observed might be a subjective one: that one result of increasing the intensity of a musical note without changing its frequency, might be to depress the pitch as estimated by ear. To determine this point I have made experiments upon myself, and on others whose perception of musical intervals was known to be reliable.

2. Let a tuning-fork mounted on a resonance-box be strongly excited by bowing, and immediately let the open end of the resonance-box be brought very close to one ear, the other ear being preferably closed. After a second or so, let the fork and box be moved away from the ear and held at arm's length, then brought close to the ear again, and so on, backwards and forwards, two or three times. If there is any

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[*] Read March 22, 1895.

subjective depression of pitch accompanying increase of loudness without change of frequency, the fork will appear to be lower in pitch when close to the ear and higher when further away, the effect becoming less marked as the vibration gradually dies down. This is what observation shows to be actually the case, and it is evidently nothing of the nature of a Doppler effect with which we are here concerned. In the first place, the motion of the fork from one position to the other may be made quite slow; and in the second place, the difference of pitch is observed, *not* between the fork approaching and the fork receding, but between the nearer and further positions of the fork.

3. In some of these observations a fork giving the note *c'* (256 complete vibrations per second) has been used, the effect with forks of higher pitch being less marked. When the vibration was made as strong as possible by means of bowing, the lowering of pitch was found to amount to a full semitone (15 : 16). Mr. Womack, Prof. Ramsay, and Dr. G. F. McCleary, who repeated the experiment, all agreed pretty nearly with my estimate: in each case the greatest apparent flattening observed was as much as a semitone.

With a large fork giving *c* (one octave lower) the effect was more striking. In this case the fork with its resonance-box was too unwieldy to be moved bodily to and fro, so it was allowed to stand on a table while the observer's head was lowered so as to bring one ear opposite to the opening of the resonance-box at a distance of a few inches. Thus the fork was heard with great intensity, while on raising the head through half a metre or so the loudness was greatly diminished. Here the lowering of pitch due to the greatest intensity of vibration which I could excite in the fork amounted usually to a minor third (5 : 6) or even more. Thus, repeating the experiment on different days, I have estimated the interval sometimes as rather more and sometimes as rather less than a minor third. Mr. Womack heard something between a minor and a major third ; Professor Ramsay a full tone ; Dr. McCleary more than a minor third.

4. Before saying more concerning the observations, it will be convenient to mention a physiological theory by which I have attempted to account for the observed effects. Helm-

holtz's discussion of the vibration of the basilar membrane in the cochlea is applicable only to infinitesimal amplitudes, inasmuch as all his equations of motion are linear, and though the introduction of terms of higher order would have made the investigation very lengthy and an exact solution impossible, it is not difficult to see on general grounds what modification of the sense of pitch is to be expected from increased loudness. If the basilar membrane may be regarded as being stretched with a finite tension in the direction of its breadth, and as having no appreciable tension in the perpendicular direction, then Helmholtz shows that it will be vibrationally equivalent to a series of strings stretched side by side and unconnected with one another. For shortness, I shall speak of the membrane as if it actually consisted of such separate strings, and thus, following Helmholtz's theory, we are to suppose that a disturbance of given period reaching the ear excites the strongest resonance in those strings whose natural period is most nearly the same. Now when a string is vibrating freely with finite amplitude, the period of its vibrations is shorter than if the amplitude were infinitesimal; and we are accordingly led to enquire whether a periodic force of considerable intensity would not excite the maximum resonance in those strings whose natural period *for some finite vibration-amplitude* was most nearly the same.

5. As sufficiently representative of our case we may take a system with one degree of freedom, in which the positional force contains a term proportional to the cube of the displacement from equilibrium, as well as one proportional to the first power*, the equation of motion being accordingly written

$$\mathrm{F} = m\ddot{x} + k\dot{x} + hx\left(1 + \frac{x^2}{a^2}\right), \quad . \quad . \quad . \quad . \quad (1)$$

where F is the external force impressed on the system, $x$ is the displacement from the equilibrium position, and $m, k, h, a$ are real constants.

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* Terms of even degree would imply that the free vibrations were not symmetrical with respect to the equilibrium position, and would therefore be absent in the case of a stretched string, which we have supposed to agree pretty nearly with the physiological case.

If we take F to be a simple harmonic function of the time whose character has been maintained long enough for the whole motion to have become periodic, the value of $x$ will be expansible in a Fourier's series in which the constant coefficients have to be determined. But the expressions thus obtained are very unwieldy; and it will therefore be more convenient to treat $x$ instead of F as a simple harmonic function of the time. It is not easy to say definitely which assumption corresponds most nearly with the actual case, and from what follows I think it will be evident enough that whichever case we consider the general conclusions would be much the same.

6. If we put, then, $x = \mathrm{B}\cos pt$,

the expression for the impressed force is

$$\mathrm{F} = -\mathrm{B}mp^2\cos pt - \mathrm{B}kp\sin pt + \mathrm{B}h\left(\cos pt + \frac{\mathrm{B}^2}{a^2}\cos^3 pt\right);$$

so that

$$\frac{\mathrm{F}}{\mathrm{B}} = \left\{-mp^2 + h\left(1 + \frac{3}{4}\frac{\mathrm{B}^2}{a^2}\right)\right\}\cos pt - kp\sin pt + \tfrac{1}{4}h\frac{\mathrm{B}^2}{a^2}\cos 3pt.$$

Let $\mathrm{F}_1$ denote the first harmonic term of F (that is, the sum of the terms in $\cos pt$ and $\sin pt$), while $\mathrm{F}_3$ denotes the term in $\cos 3pt$. Then, since

$$\dot{x} = -\mathrm{B}p\sin pt,$$

we have

$$\frac{\mathrm{F}_1^2(\text{max.})}{\dot{x}^2(\text{max.})} = \frac{1}{p^2}\left\{-mp^2 + h\left(1 + \frac{3}{4}\frac{\mathrm{B}^2}{a^2}\right)\right\}^2 + k^2.$$

When $m$, $k$, $h$, $a$, and B are given, the minimum value of the right-hand side corresponds to

$$mp^2 = h\left(1 + \frac{3}{4}\frac{\mathrm{B}^2}{a^2}\right) > h.$$

Also

$$\frac{\mathrm{F}_3^2(\text{max.})}{\dot{x}^2(\text{max.})} = \frac{1}{16p^2}h^2\frac{\mathrm{B}^4}{a^4},$$

which diminishes continually as $p^2$ increases. Hence in general terms we may say that to produce a given amplitude of velocity requires the least amplitude of impressed periodic force when the periodic time of the force is *somewhat shorter* than would be the natural period of the system for infinitesimal vibrations if the frictional term were abolished. And returning to the case of our strings, we may infer that a similar result will hold good. Hence a force of given finite amplitude will excite in a given string the greatest amplitude of velocity when the period of the force is somewhat shorter than the "natural" period of the string, and hence when a periodic disturbance of finite amplitude reaches the ear, the string whose resonance is excited most strongly will have a "natural" period *longer* than the period of the disturbance.

7. For example, let the note *c* be sounded with very small intensity, and let that part of the basilar membrane which responds most strongly be called the *c*-string. If then the same note *c* is made to sound close to the ear with considerable intensity, the strongest resonance will be excited no longer in the *c*-string, but in some string of longer natural period, such as the B♭-string. Now according to Helmholtz's theory of sound-perception our estimate of pitch depends entirely on localization of the most strongly agitated portion of the basilar membrane, so that in the case just considered, when the note *c* was made to change from a very small to a very much greater intensity, we should expect to hear not only an increase of loudness, but also a lowering of pitch.

8. At the same time it is not to be supposed that the agitation of the "*c*-string" is lessened when the intensity of the note *c* is augmented. The effect must necessarily be in the other direction, so that such a note powerfully sounded close to the ear must perceptibly excite a tract of the basilar membrane corresponding to a considerable *range* of pitch (the place of maximum disturbance being probably not far from the middle of this range).

9. We must even suppose that an increase in the intensity of a note without change of frequency causes the "range of stimulation" (as we may call it) to extend to patches *a little higher* than before, as well as to those a good deal lower.

10. In connexion with § 8 it may be remarked that, when the ear is kept close to the resonant cavity of a strongly-vibrating *c*-fork, the impression of pitch obtained is far from being very definite. One pitch or another within an appre-

ciable range may be heard by a mere effort of attention. On the other hand, a more definite impression is obtained on alternating between smaller and greater intensities of the same note. Thus, on raising or lowering the head, as mentioned in § 3, the interval between the soft note and the loud note may appear at first to be about a minor third, when the fork is sounding strongly. As the amplitude of vibration dies down, the interval diminishes, and it is possible to say pretty definitely when it is just a whole tone, and when it is only a semitone; until, as the note in either position of the head becomes nearly inaudible, the apparent difference of pitch is obliterated.

11. If the orifice of the ear remote from the fork is left open, the sound reaching that ear will be less intense than is heard by the other ear, and the corresponding pitch will be higher. Though of course beats are entirely absent*, it might be thought that two distinct pitches would be heard simultaneously, but this requires a distinct effort of attention. The general impression is of a pitch intermediate between those which would be heard by the two ears separately, so that on closing the further ear a distinct lowering of pitch takes place. For this reason the effects described in § 3 are most marked when the less stimulated ear is kept closed.

12. I have not yet mentioned an effect noticed by an observer in whom hearing with one ear was not normal. With the less sensitive ear the usual effect was reversed; that is, on bringing the ear close to the resonance-cavity of the *c*-fork, the pitch, instead of falling, appeared to rise by about a semitone. Even taking § 9 into account, this result seems rather anomalous.

13. Though variations of pitch accompanying variations of loudness must frequently have been observed, the physiological influences at work do not appear to have been suspected †.

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* In the discussion Prof. S. P. Thompson suggested that, if the observations were valid, beats should occur between the notes heard by the two ears; but a consideration of the physical conditions will show that nothing of this kind is to be expected.

† For example, Lord Rayleigh mentions ('Theory of Sound,' 2nd ed. vol. i. § 67) that "tuning-forks rise a little, though very little, in pitch as the vibration dies away."

And yet these subjective influences must be by no means negligible in the case of wind-instrument players; and even from players of stringed instruments I think I have heard that it is easier to judge of another player's intonation than to be quite certain about one's own. On the other hand, as regards the tuning of the intervals of consonant chords, it must be remembered that the actual criterion is usually the obliteration of beats, so that on this point the judgment is not disturbed by a small subjective uncertainty in the estimation of pitch. I have also convinced myself that, when harmonic upper partials are present, the sense of tonality is largely dependent upon them; and harmonics from their higher pitch and generally feebler intensity will suffer less subjective repression of pitch than the fundamental.

## II. *Objective Demonstration of Combination-Tones.*

14. When two notes differing in frequency are powerfully sounded in the neighbourhood of one another, secondary tones are produced, of which the most prominent have frequencies respectively equal to the sum and difference of the frequencies of the parent tones. It has been maintained by some writers that these secondary tones are purely subjective, and have no existence external to the ear, and the following experiment was designed to show that in some cases at least the first difference-tone has a real physical existence. If the vibration of the air external to the ear has really a component of the frequency in question, we must suppose this component to have arisen from a failure of the principle of superposition, that is, from the circumstance that as the parent vibrations are of considerable amplitude, the equations of motion cannot be regarded as sensibly linear; and accordingly it is to be expected that if two sources of sound are brought closer together, the intensity of the difference-tone will increase. I have used two stopped organ-pipes of white metal giving the notes $e'$ and $g'$, the difference-tone being consequently C. The pipes are connected to a well-weighted organ-bellows by flexible rubber tubes, and the distance between them can be varied at will from a few feet to a couple of inches (the walls of the two pipes being then in contact). It is best for the listener to be stationed in a distant room, so that the sound

which reaches him is only of moderate intensity, while the comparatively small distances through which the pipes are moved does not appreciably affect the sounds which they individually send to his ear. The bellows being filled, the sounding pipes are held alternately far apart and near together, and each time, as they nearly approach one another, the difference-tone $C_1$ is heard to boom out with greatly increased intensity. From this, I would suggest, we are to infer that the difference-tone has a real objective existence.

(Further experiments have *not* confirmed this result. Even Prof. Rücker's very sensitive arrangement of interference-bands failed to show any objective difference-tone from the two organ-pipes, suitably tuned. An attempt will be made to deal with the subject more fully in a subsequent paper.)

## DISCUSSION.

Mr. EDSER mentioned that Dr. Burton had suggested an explanation of the production of objective tones in the use of the siren which depends on the production of the tones in the wind-chest of the instrument itself, when two rows of holes are simultaneously opened. They had made an experiment which seemed to show that the above explanation was incorrect, for on connecting together the wind-chests of two sirens, fixed on the same spindle, by means of a short length of wide metal tubing, no effect was observed on the bands when the two notes were produced on different instruments having what was practically a common wind-chest.

Prof. EVERETT (in a letter) said he considered the experiments described in the paper proved conclusively the objective existence of the summation-tones as distinguished from the supposed beat-tones. He had lately been investigating the pitch of the loudest combination-tone obtained when two notes having frequencies as 3 to 5 are sounded. Is the frequency of this tone 2, *i. e.*, the first difference-tone, or is it 1, which corresponds to the first term of the Fourier series for the periodic disturbance? In the chords 2 to 3, 3 to 4, 4 to 5, &c., the difference of the two integers being unity, the first difference-tone is identical with the first Fourier tone. Where the difference of the two integers which express the chord is not unity, then the writer considers that experiments he has made with strings and pipes show that the first Fourier term is usually the only combination-tone that is audible.

Prof. S. P. THOMPSON considered that care should be taken to define what we mean by the subjective or objective existence of a note, and recommended the use of the term "ear-made tone." There are two very delicate methods which have already been employed for detecting the existence of a given note in the air:—1. The formation of ripples on a soap-film stretched over the opening of a resonator tuned to the required pitch (Sedley Taylor). 2. The sounds produced in a telephone connected to a microphone placed on a thin elastic membrane stretched oves the neck of the resonator (Lummer). It was very important to limit our acceptance of the demonstration of the objectivity of combination-tones given by the authors of the paper to the case actually proved, *i. e.*, to tones produced by the polyphonic siren; it did not necessarily follow that if pure tones produced by tuning-forks were used, the same results would be obtained. A number of experiments had been made by Zantedeschi in 1857, in which two notes were sounded, and skilled musicians were asked to record their impression of the third tone present. In 75 per cent. of the cases the note recorded was the difference-tone. In the remaining 25 per cent. it corresponded to König's beat-tone. König himself had never heard the summation-tone in the case of lightly bowed forks. Voigt, in a theoretical paper, has shown that if there are two disturbances, whose mean kinetic energy differ, the Helmholtz tones well be produced; but that if the mean kinetic energy of the two disturbances are equal, the Helmholtz effects soon die out, and you get beat-tones or beats. He (Prof. Thompson) considered that Dr. Burton had allowed his perception of tone to be governed by the quality of the note, and that the apparent lowering of pitch was due to the variation in the intensity of the overtones present.

In reply to Prof. Thompson, Dr. BURTON said he did not merely perceive a lowering of pitch, but he was able to estimate the change in pitch and say at what instant, as the vibrations of the fork died out, the lowering amounted to a tone or half a tone, &c.

Mr. BOYS said he found that by careful attention he could apparently persuade himself that the note in Dr. Burton's experiment was lowered or raised in pitch, or that it remained unaltered. A similar effect in the case of the eye could be obtained with a stereoscopic picture.

The CHAIRMAN considered that while Helmholtz's explanation of the production of combination tones might be real, it did not follow that this explanation gave the sole cause of their formation. In particular Helmholtz does not explain why the tones should only be produced by some sources of sound.

Prof. RÜCKER, in his reply, said he did not deny the existence of König's beat-tones; in fact, he had heard them. They did not lay much stress on the negative result of the experiment they had made to test the objective existence of these beat-tones.

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## XXXVIII. *Tests of Glow-Lamps, and Description of the Measuring Instruments Employed.* *By* Prof. W. E. AYRTON, *F.R.S., and* E. A. MEDLEY*.

THE conditions under which the glow-lamp can be most economically used have attracted considerable attention since a paper entitled "The Most Economical Potential Difference to employ with Incandescent Lamps" was read before the Physical Society in February 1885† by Professor Perry and one of the authors of the present communication. In this paper they stated that it was well known, from experiments made by their students in 1880, and from results published in 1881 by Lord Kelvin, then Sir William Thomson, as well as from subsequent experiments, that the light obtained from an incandescent lamp increased much more rapidly than the power expended in it; or, that the number of candles produced per watt of power expended in the lamp increased as the filament became hotter. But it was pointed out in the paper in question that such experiments by themselves gave no idea of the commercial value of any particular glow-lamp, because they afforded no indication of its life when run at different efficiencies, and it was known that the length of time a filament would last was the less the higher its temperature.

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* Read December 14, 1894, and January 25, 1895.

† Proc. Physical. Soc. vol. vii. p. 40; Phil. Mag. April 1885, p. 305.

They then proceeded to show that the cost of lighting per hour per candle could be divided into two parts, viz., the cost as to lamp renewals and the cost as to power, the first being equal to the price of a lamp divided by the product of its life into its candle-power, and the second to the price of one watt-hour multiplied by the watts per candle. So that, if $L(v)$, $C(v)$, and $W(v)$ were the life in hours, the candle-power, and the watts per candle respectively expressed as functions of the pressure in volts kept constantly on the lamp, and if $p$ were the price of a lamp and H the price of one watt-hour, then the cost per hour per candle equalled

$$\frac{p}{L(v) \times C(v)} + H \times W(v),$$

and the value of $v$ which made this expression a minimum, they showed, was the proper P.D. to employ with the particular type of lamp.

The authors gave two methods of solving this problem defined by their equation of cost—the one a graphical method, and the other an analytical one. The graphical method consisted in drawing curves from the best experimental results then available to represent $L(v)$, $C(v)$, and $W(v)$ respectively in terms of $v$, and from these three curves finding the values of $L(v)$, $C(v)$, and $W(v)$ for many values of $v$, then, by substitution in the cost equation, data were obtained from which a last curve showing the relation between potential difference and cost per hour per candle could be drawn.

The curves on p. 45, Proc. Phys. Soc. vol. vii. 1885*, showed the results obtained when this method was applied to the case of 16 C.P. 100-volt Edison lamps, using as experimental data the results of tests, made at the Finsbury Technical College, on the relations between candles, volts, and watts, and the values of the life of this type of lamp when run at different pressures, as published by M. Foussat.

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* Phil. Mag. *tom. cit.* p. 308.

The curve AAA showed the cost per candle for lamp renewals during 560 hours when the price of a new lamp was five shillings; BBB the cost per candle for power during the same period, one horse-power for 560 hours being reckoned at £5, and CCC gave the total cost per candle for 560 hours. The ordinate of this latter curve had a minimum at about 101·4 volts.

With the analytical method, on the other hand, empirical equations were first found to represent as nearly as possible the experimental results. Thus it was found that

$$\frac{1}{\mathrm{L}(v)+\mathrm{C}(v)} = 10^{0\cdot07545\,v-11\cdot697}$$

and

$$\mathrm{W}(v) = 3\cdot7 + 10^{8\cdot007-0\cdot07667\,v};$$

therefore the total cost per hour per candle equalled

$$p\,10^{0\cdot07545\,v-11\cdot697} + \mathrm{H}(3\cdot7 + 10^{8\cdot007-0\cdot07667\,v}).$$

From this equation, using the same values for the price of lamps and power as before, it was shown that to make the cost a minimum the P.D. maintained between the lamp-terminals should be 101·1; a result in close agreement with that obtained graphically.

At the next meeting of the Physical Society a paper was read by Dr. Fleming *, in which he considered what proportion the cost of lamp renewals should bear to the cost of power in order that the total cost should be a minimum. As the result of the examination of various experiments, he showed that for any particular type of lamp the average life could be expressed as an exponential function of either the watts per candle, or of the candle-power, or of the P.D.; that is, he showed, for the lamps with which he was dealing, that

$$\mathrm{L} = \frac{\mathrm{A}}{\mathrm{W}^{\alpha}} = \frac{\mathrm{B}}{\mathrm{C}^{\beta}} = \frac{1}{v^{\gamma}},$$

where L was the life, W the watts per candle, C the candle-power, $v$ the P.D., and A, B, $\alpha$, $\beta$, and $\gamma$ constants for any

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* Proc. Physical Soc. vol. vii. p. 55; Phil. Mag. May 1885, p. 368.

particular type of lamp. Then, by substitution in the cost equation already referred to, he obtained the result that for maximum economy the cost of power must be to the cost of renewals as $\alpha\frac{\beta-1}{\beta}$ to unity. The values for $\alpha$ and $\beta$ he gave for Edison lamps as $6\frac{1}{4}$ and $4\frac{1}{6}$ respectively; so that he finally arrived at the result that, whatever the price of lamps, or of electrical energy, the pressure used must be such that the annual cost of renewals should be about 17 per cent. of the total annual cost.

In April 1888, in a paper read before the American Institute of Electrical Engineers, Mr. Howell gave numerous examples of the application of Ayrton and Perry's graphical method to the finding of the efficiency at which various types of lamps should be run to obtain maximum economy for various prices of lamps and power.

He gave a curve showing the results of his tests of Edison lamps when run at different efficiencies, but the lamps he used were so abnormally good, compared with any with which we are acquainted, that his experiments have no practical value. For example, his lamps run at 4·5 watts a candle lasted, he says, nearly 12,000 hours.

Further, Mr. Howell's paper can hardly be said to have advanced the matter beyond the point at which it was left by the considerations contained in the paper on "The Most Economical Potential Difference, &c.," read before this Society in 1885; for he took no account of the changes which more recent experiments had shown to occur in lamps during their life, and which render any results obtained by methods that disregard these changes useless for practical purposes.

Numerous experimenters had found out that there was a serious diminution in the light emitted by a lamp as it grew old, and also a very considerable rise in the watts consumed per candle. Further, there was evidence to show that the shape of the curve between candle-power and time was not the same for different pressures; so that it had come to be recognized that, in order to determine the P.D. at which lamps should be run, it was useless to make a comparison merely between the efficiency of lamps when new and the number of hours they will last at various voltages.

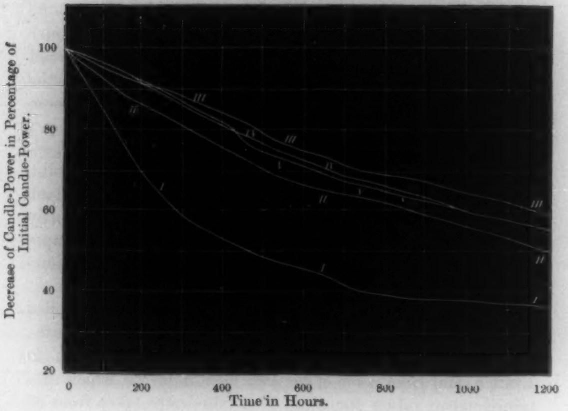
Moreover, this falling-off in the quality of a lamp as it ages led people to consider another point, viz., Might it not be possible, in consequence of this deterioration, for a lamp to be economically dead before the filament had actually broken? For the increased cost of the current required, compared with the light given out, might more than overbalance the expense of replacing the lamp with a new and, therefore, more brilliant one.

Before describing the results which we have obtained regarding this interesting question of the existence of a point, called by the Americans the "smashing point," beyond which a lamp cannot be economically used, it will be well to shortly indicate the general conclusions to which previous experimenters have been led from tests on the modern glow-lamp.

In November 1892 Mr. Feldman published a table compiled from the results of tests made by Prof. Thomas and Messrs. Martin and Hassler in America, by M. Haubtmann in France, and from some of his own measurements, which contained mean values for more than 500 lamps taken from 28 different factories and representing 49 different types. He divided the lamps into five groups according to their initial efficiencies, and gave for each group the average candle-power in per cent. of the initial candle-power and the average watts per candle at every hundred hours in the lives of the lamps. The curves in figs. 1 and 2 are drawn from the figures given in this table, fig. 1 showing the candle-power and fig. 2 the watts per candle as the lamps grow old. The numbers I., II., III., IV., and V. on the curves refer to the initial efficiencies of the lamps whose behaviour the curves illustrate, and, as seen from the table on fig. 1, the curves marked I. are drawn from results obtained from lamps which initially required from 2 to 2·5 watts per candle; for curves marked II. the initial consumption was 2·5 to 3 watts per candle; for curves III. from 3 to 3·5; for curves IV. from 3·5 to 4; and for curves V. above 4 watts per candle.

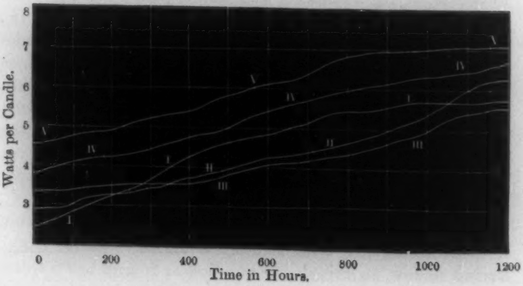
These curves show that the fall in candle-power varied from 40 to 65 per cent. in 1200 hours, or, rejecting lamps having as low an initial consumption as from 2 to 2·5 watts per candle, Mr. Feldman's curves would lead us to expect

Fig. 1.—Tests of American and European Lamps.



| Curves marked | Initial Watts per Candle. |
|---|---|
| I. .................. | From 2·0 to 2·5 |
| II. .................. | From 2·5 to 3·0 |
| III. .................. | From 3·0 to 3·5 |
| IV. .................. | From 3·5 to 4·0 |
| V. .................. | Over 4. |

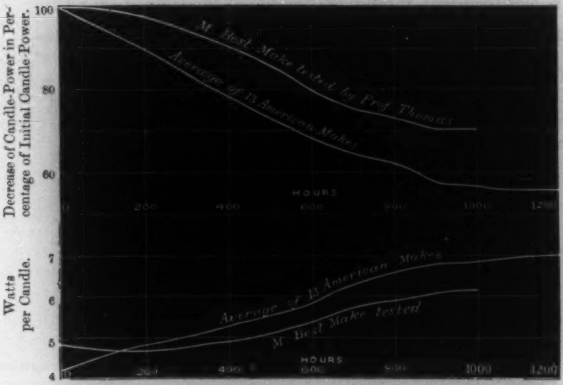
Fig. 2.



that the candle-power of an average lamp would fall about 40 per cent. in 1000 hours.

From the curves marked A in fig. 3, which give the results of Professor Thomas' tests made in 1892 on 127 lamps of 13 American makes, it can be seen that the average American lamp of that date dropped about 43 per cent. in candle-power in 1000 hours, the watts per candle in the same time rising from 4·2 to 6·9. The curves marked M on the same figure show the results obtained from the best make of lamp tested by Professor Thomas; the average of the 10 lamps tested showed a drop of 30 per cent. in candle-power in 1000 hours, and a rise from 4·8 to 6·1 in watts per candle.

Fig. 3.—Prof. Thomas' American Tests.



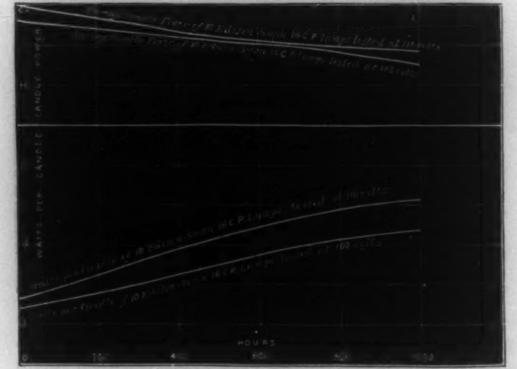
In September 1892 M. Haubtmann published tests on many European makes of lamps. The curves in fig. 4 show the results he obtained from testing twenty 16 C.P. Edison-Swan lamps, ten at 102 and ten at 110 volts. Those run at 102 volts showed a drop of about 30 per cent. in candle-power in 1000 hours, the watts per candle rising in the same time from 3·27 to 4·4; the lamps run at 110 volts in 1000 hours dropped 28 per cent. in candle-power and rose from 3·35 to 4·58 watts per candle.

If, now, in the light of the knowledge obtained from these experiments, we look at the equation of cost quoted in the beginning of this paper, we see that some changes must be made in it before it expresses the truth. As originally given it was :—Cost per hour per candle equals

$$\frac{p}{\mathrm{L}(v) \times \mathrm{C}(v)} + \mathrm{H} \times \mathrm{W}(v);$$

but, as neither the candle-power nor the watts per candle remain constant throughout the life of the lamp, $\mathrm{L}(v) \times \mathrm{C}(v)$

Fig. 4.—Tests by M. Haubtmann on 20 similar 16 Candle-Power Edison-Swan Lamps, 10 of which were run at 110 volts and 10 at 102 volts.



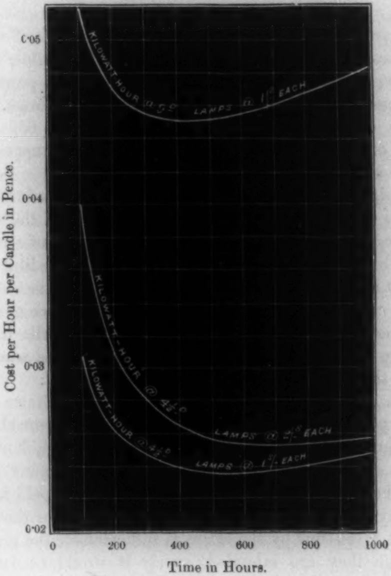
does not give the total candle-hours obtained during the lamp's life, and neither does $\mathrm{H} \times \mathrm{W}(v)$ give the true cost of power per hour per candle. The equation must, therefore, be written :—Cost per hour per candle equals

$$\frac{p}{\text{total candle-hours}} + \mathrm{H} \times \textit{average} \text{ watts per candle.}$$

Exactly what these changes in the equation mean will be best shown by working out the results for a particular type of lamp, and for this purpose we have chosen the American make tested by Professor Thomas, the life curves of which are shown marked M in fig. 3.

It is clear, from these curves, that knowing the initial candle-power, in this case about 12·5, we can calculate at any time during the life of a lamp the total candle-hours obtained and the average watts consumed per candle during that time, and by substituting these quantities in the equation of cost we can find the cost per hour per candle averaged over the number of hours considered.

Fig. 5.—Cost Curves calculated for American make M in fig. 3.



The curves in fig. 5 show the results we have obtained when these calculations are made at different times in the life of a lamp, and for different prices of lamps, and of power. In calculating the figures from which the bottom curve is plotted, we have taken the cost of a new lamp as one shilling, and the price of a Board of Trade unit as 4½*d.*, and, as seen, the ordinate of this curve reaches a minimum at about 600 hours, when the cost per hour per candle has dropped to 0·0235 pence. Beyond this point the curve begins to ascend; that is, when a new lamp costs one shilling, and a kilowatt-hour 4½*d.*, and lamps whose life-histories are truly represented by the curves M in fig. 3 are employed, the cost of obtaining light is least if the lamps are used for 600 hours only, because after that time their diminished quality more than overbalances the cost of renewing.

A change in the price of lamps does not much affect the economical life, as is shown on fig. 5 by the middle curve, which we have calculated for the same price of power but on the assumption that a new lamp costs two shillings. The ordinate of this curve has a minimum value at 650 hours instead of at 600 hours, when a new lamp was supposed to cost one shilling only.

The higher the price paid for energy the more important does this question of economical life become, and the sooner is it necessary to discard lamps, because the cost of renewals bears a less proportion to the total cost. This is illustrated in fig. 5 by the top curve, to obtain which we have assumed that the cost of energy was 9*d.* a unit, and the price of a new lamp one shilling. Now the minimum point falls to 430 hours instead of being at 600, at which it stood when the price of the Board of Trade unit was taken as 4½*d.*

When cost curves, like those in fig. 5, are drawn for a worse type of lamp, the minimum point becomes more sharply defined and is reached earlier. It might be urged, however, that all such curves merely indicate for how many hours lamps should be used in order that the price paid for the light may be a minimum, but that, if at the end of that time the light given out by the lamps is sufficient for the purpose for which they are intended, surely it would be folly to discard them. The answer to this is, that the lamps employed were of too high candle-power for the necessary illumination, and what should be done is to throw away the nominally higher candle-power lamps that have deteriorated and replace them with new *lower* candle-power lamps.

When, therefore, the special investigation which forms the subject of this paper was commenced at the end of 1892, there was good reason for expecting, first, that with any type of glow-lamp a certain number of hours could be experimentally determined at the end of which it would be economical to discard lamps even when the price of a Board of Trade unit was as low as 4½*d.* ; secondly, that it was only economical to run lamps at the pressure marked on them for one particular price of electric energy.

As Edison-Swan lamps were the only lamps that could be legally used in this country in 1892, and as a pressure of 100 volts was one very commonly employed for electric lighting, we decided to experimentally find out what was the most economical pressure to maintain between the terminals of nominal 100-volt 8-candle lamps of this make, and what was the length of their economic lives for different prices of a Board of Trade unit.

As it is well known that the lives of filaments are considerably affected by the steadiness of the pressure between their terminals, it was decided to run the lamps from a battery of storage-cells, and to arrange that the pressure when on the lamps should not vary by as much as one tenth per cent. The capacity, however, of the cells at the Central Technical College which could be entirely set on one side for this investigation and used for running 100-volt lamps from five o'clock every evening to nine or ten o'clock the next morning for five nights of the week, only allowed of nine 8 C.P. lamps being dealt with at a time. The nine lamps were divided into three groups, each containing three lamps, and a perfectly constant, but different P.D. was maintained between the terminals of the lamps in each group.

When our experiments were begun it was known that the price of lamps would fall in the autumn of 1893, therefore it was considered hardly probable that any economy would be gained by running the lamps at less than their normal pressure. Hence we decided to run the three groups at 100, 102, and 104 volts respectively. The tests, however, soon proved that no economy could be gained by running these lamps at as high a pressure as that of 104 volts, and so the group running at that pressure was changed for one running at 101 volts.

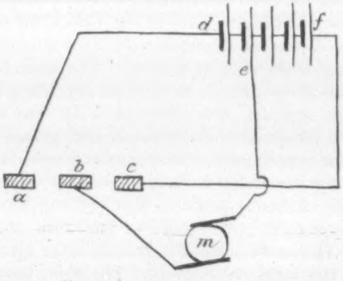
The pressure of the storage-cells which supplied the lamps with current diminished, of course, during the night, so that it was necessary to introduce between the cells and the lamps a variable resistance which could be altered to keep the pressure on the lamps constant within one tenth per cent., and to avoid constant attention it was also necessary that this resistance should be automatically controlled.

As no automatic regulator could be purchased which would keep the pressure throughout the night within one tenth per cent. of the desired value, it was necessary to construct such an instrument.

The apparatus which we employed for this purpose resembled generally the one described in a paper on "The Working Efficiency of Secondary Cells" by Messrs. C. G. Lamb, E. W. Smith, M. W. Woods, and one of the authors of the present communication, *see* Journ. Inst. Elect. Eng. vol. xix. 1890.

A variable resistance, consisting of four platinoid wires winding on and off a brass roller, was placed in the main circuit between the cells and the lamps. This resistance was geared to a permanent magnet Gramme-motor, the electrical connexions of which are shown in fig. 6. *d e f* was a battery of five storage-cells to the centre *e* of which one brush of the motor *m* was connected, the other brush being joined to the middle cup *b* of a three-way mercury switch *a b c*. The two

Fig. 6.



outer cups *a* and *c* of this switch were connected with the two ends *d* and *f* of the battery.

It is clear from the figure that the motor revolved one way or the other according as *a* and *b* or *b* and *c* were connected.

A "set up" d'Arsonval galvanometer in series with a resistance was placed across the two points in the main circuit between which it was desired that the pressure should remain constant. To the coil of this galvanometer was attached a pointer ending in a platinum tip which worked between two platinum contacts. The phosphor-bronze strip by which the coil of the d'Arsonval was suspended was twisted several times, so that when the pressure on the lamps was correct the tip of the pointer rested midway between the contacts. If, however, the pressure rose by one tenth of a volt the pointer was deflected and made to touch one of the contacts, and so to complete the circuit of an electromagnet; this, by closing one side of the mercury switch (fig. 6), started the motor, which increased the resistance in the main circuit until the pressure was correct again.

Exactly the opposite happened if the pressure fell, the pointer touched the other contact, the other side of the mercury switch was closed, and the motor working in the reverse direction reduced the resistance between the cells and the lamps.

The pointer was kept from sticking to its contacts by a light wooden hammer which tapped the case of the galvanometer when the motor revolved.

By means of this apparatus it was possible to keep the pressure constant to within at least one tenth per cent.

For many nights the action of this regulator was watched pending the arrival of a recording voltmeter, but the recording voltmeter not being forthcoming, and staying up all night, even for four times a week, interfering much with our work during the day, we decided to construct an automatic check on the automatic regulator.

In series with the first galvanometer was placed a second working in exactly the same way, but with its contacts so far apart that its pointer only touched them for a rise or fall of half a volt in the pressure on the lamps. When for any reason such an alteration took place, the pointer of this second galvanometer, by touching one of its contacts, completed the

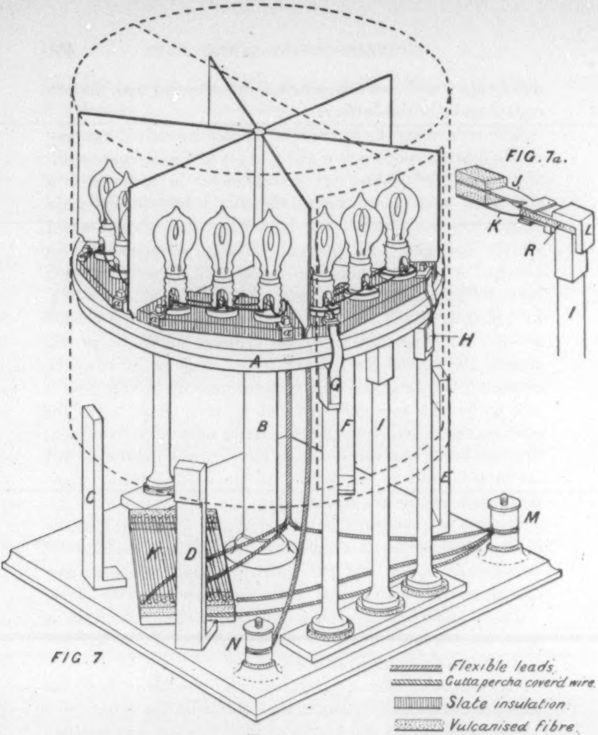
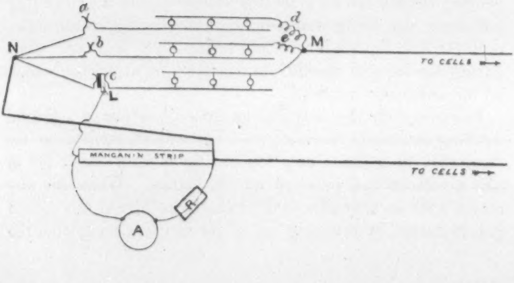


FIG. 7a.
J
K
R
L
I
A
B
C
D
F
G
H
I
I
E
K
M
N
Flexible leads
Guttapercha coverd wire
Slate insulation
Vulcanised fibre

FIG 7.

Fig. 8.


a
b
c
d
e
N
M
L
TO CELLS
MANGANIN STRIP
TO CELLS
R
A

circuit of an electromagnet; this attracted a piece of soft iron which opened a mercury switch and put out the lamps, and at the same time by stopping a clock indicated the time at which the irregularity took place.

Besides acting as a check on the regulating apparatus, this automatic cut-out worked whenever the pressure rose on a lamp breaking, and so made it possible to tell the exact life of the broken filament.

The lamps being tested were arranged in the special stand shown in fig. 7. The circular plate A, which could be turned on the centre pillar B, was divided into six compartments by the radial divisions shown, and the nine lamps simultaneously tested were placed in three of these compartments, which were coloured a dead black inside. The whole was covered up with an outer tin case, drawn in broken lines, which was fixed to the uprights C, D, E, F, and had an opening in front through which any one of the groups of lamps could be seen when turned into position.

When photometric measurements were not being made, the top of the case was left open to let out the heat.

The arrangements for measuring the current and for bringing it to the lamps are sketched in fig. 8. M and N are the main terminals of the lamp-stand, corresponding with M and N in fig. 7. From M the current, after passing through the resistances *e* and *d*, for the two groups run at lower pressures, went through the lamps and reached the terminal N by means of the copper springs *a*, *b*, and *c*.

When, however, a group of lamps was turned into position for photometric measurements its copper springs *c* (J and K in fig. 7*a*) were separated by a piece of brass L backed with insulation (R in fig. 7*a*), and so the current of the group was diverted through a thick wide strip of manganin, this strip being shunted with an Ayrton and Mather d'Arsonval galvanometer, A, in series with a resistance R, as seen in fig. 8.

This combination of galvanometer, resistance R, and manganin strip was calibrated by direct comparison with a Kelvin balance, and the resistance R was so adjusted that one ampere produced a deflexion of 500 divisions, each of about a millimetre in length. Variations of current during the experiments could be read to $\frac{1}{3000}$ of an ampere if required, and the current was known accurately in Board of Trade amperes to $\frac{1}{1000}$ of an ampere.

The results of frequent comparisons between an ampere as read off on the direct-reading transparent scale and an ampere as measured with the Kelvin balance, which was also screwed down permanently in position, never showed a difference as large as 1 part in 1500 between September 1893 and August 1894.

The positive and negative terminals of each group of lamps were connected respectively with two squares of brass *a*, *a* (fig. 7) let into the slate bed on which the group was mounted. Two brass springs, G, H, permanently connected with an Ayrton and Mather reflecting electrostatic voltmeter, the motion of the needle of which was damped by moving in a magnetic field, pressed on the brass squares *a*, *a* of whichever group of lamps was brought to the front of the stand.

The zero of the voltmeter was so arranged that the transparent scale, which was direct-reading, was nearly uniformly divided from 50 to 120 volts, each division of about 1·5 millimetre representing 0·2 volt, so that it was easy to read the deflexion to within 2 parts in 10,000.

The electrostatic voltmeter was frequently calibrated, and the maximum change in sensibility between July 1893 and August 1894 did not exceed 0·2 per cent. This change, although small, is fully accounted for by the variation in the zero, since the instrument did not possess the delicate zero adjustment of the later specimens of this type of voltmeter.

The standard of light we used was a two candle-power Methven screen fed with *pentaned* gas, and against this a ten candle-power Bernstein glow-lamp was standardized to give five candles, the Bernstein lamp being employed for the actual comparison with the Edison-Swan lamps.

One of the objects of employing this Bernstein lamp was to test whether or no a convenient and trustworthy standard of light could be obtained by using a low-voltage lamp with its filament at a comparatively low temperature. From this point of view, however, the results were not very satisfactory, as at the end of some sixty hours of life the lamp had blackened heavily. This secondary standard was of course tested very frequently—as a rule, every time it was used.

For the last few hundred hours of our tests an 8 C.P. 100-volt Edison-Swan lamp running at five candles was used as an intermediate standard of light, and after the first few hours it gave very fair results, the current required to produce exactly five candles dropping in almost a straight line from 0·3893 to 0·3867 ampere in two hundred hours. It is probable, for reasons which will be shortly apparent, that an even better result would have been obtained if the lamp had been run for some fifty hours at its normal brilliancy before it was used as a standard of light.

For measuring the light a Lummer-Brodham photometer was used, and proved itself a very convenient instrument. The lamp-stand was fixed at the end of a three-metre photometer bench, the actual distance between the standard and the Edison-Swan lamps being 319·5 centims.

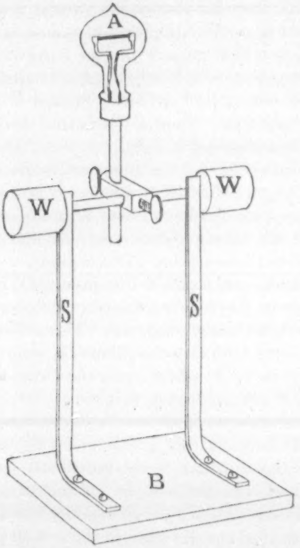
Some difficulty was found at first in measuring the candle-power owing to the very considerable difference in colour between the lights being compared. This difficulty was considerably reduced by fixing the Bernstein lamp to the spring frame shown in fig. 9, where A is the lamp, S, S are steel springs, and W, W are leaden weights.

When measurements of the candle-power were being taken, the Bernstein lamp was set gently swinging backwards and forwards in the direction of the bench, and the effect thus easily produced was found to be an improvement on that usually obtained by moving the photometer first a little on one side, and then a little on the other, of the neutral point. After some practice the use of this contrivance enabled us to make measurements of the candle-power which did not differ from each other by more than 0·3 per cent.

The first point noticed after starting the tests was that candle-power, current, and candles per watt all *rose* as the lives of the lamps increased; and as we were not prepared, from the published accounts of experiments previously made on glow-lamps, to expect any such result, we thought it might be due to some error in our measurements. We therefore made a number of tests to satisfy ourselves that this was not the case.

A current nearly twice as large as the maximum required to be measured was sent through the manganin strip for several hours, but the deflexion of the d'Arsonval galvanometer for a given current was not altered, so that the effect was certainly not due to the heating of the strip or galvanometer-coil.

Fig. 9.



As the voltmeter was connected with the terminals of the lamp sockets and not with the terminals of the lamps themselves, we tested whether any resistance was introduced by the sockets, or whether any alteration occurred when they got warm after the lamps had been glowing for some hours. An old lamp was taken and wires soldered to its terminals, and also to the terminals of the socket into which it was screwed, and, by measuring as nearly simultaneously as possible the pressures on the lamp and on the socket terminals under various conditions as to heat and position of lamp, we proved that the resistance of the socket and contacts was never perceptible.

There seemed, therefore, no reason to doubt the results already obtained; but as the accuracy with which the candle-power could be measured had increased with practice and with the introduction of the swinging frame, we decided after 110 hours of testing to start again with new lamps.

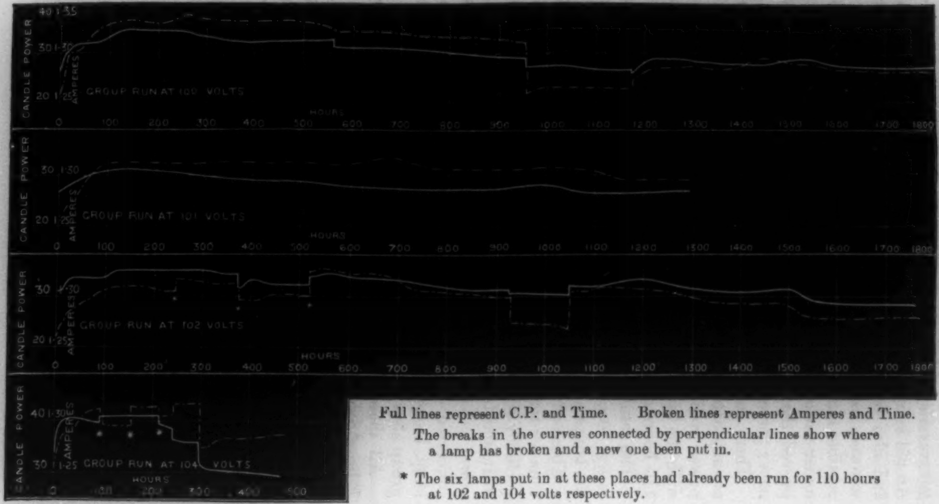
The results obtained in these preliminary tests are shown in fig. 10*a*, the curves in fig. 10 being those obtained from the lamps subsequently tested.

These curves show the variation of light and current with time for four groups of lamps between the terminals of which perfectly constant P.Ds. of 100, 101, 102, and 104 volts were maintained respectively, the full lines representing candle-power and the dotted lines current. The breaks in the curves connected by vertical lines indicate the times at which a lamp broke and was replaced by a new one, so that each group always consisted of three lamps.

All these curves show that the light given out by these Edison-Swan lamps was *greater* after they had been glowing for some time than it was when the lamps were new; also that even just before the filament of one lamp in a group broke, the total light given out by the group of three was greater than when the lamps were new. This is a totally different result from that obtained in earlier tests, as illustrated in figs. 1, 2, 3, and 4, which showed that a considerable deterioration in candle-power always took place after lamps had been running for some time. Further, while the globes of earlier lamps were always much blackened, even after a run of a few hundred hours, and so became comparatively useless long before the filament broke, the Edison-Swan lamps which we have been testing showed hardly any blackening, even when the filaments lasted for over 1300 hours.

The highness of the average candle-power of Edison-Swan

Fig. 10.—Life Tests on Edison-Swan 8 C.P. 100-volt Lamps run at Various Voltages.



Full lines represent C.P. and Time. Broken lines represent Amperes and Time.

The breaks in the curves connected by perpendicular lines show where a lamp has broken and a new one been put in.

* The six lamps put in at these places had already been run for 110 hours at 102 and 104 volts respectively.

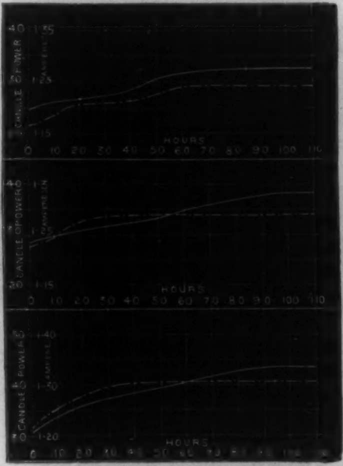
lamps marked 100–8 after they have been run for some time at 100 volts, is corroborated by the figures in the following table, which gives the results of the measurements of the candle-power and the watts per candle of eleven 8-candle 100-volt lamps which had been run from the mains of the Notting-Hill Electric Lighting Co. As these lamps had been used in different rooms of a dwelling-house, it was impossible to say for how many hours they had been run, but the time probably varied from about 200 to 600 hours, and at any rate none of them were new.

Fig. 10 *a*.—Preliminary Tests on Edison-Swan 8 C.P. 100-volt Lamps run at Various Voltages.

Group of 3 Lamps marked 100–8 run at 100 volts.

Group of 3 Lamps marked 100–8 run at 102 volts.

Group of 3 Lamps marked 100–8 run at 104 volts.



Full lines represent Candle-Power and Time,
Broken lines represent Amperes and Time.

The measurements were taken at 100 volts, and Harcourt's pentane burner was the standard of light used.

| Candle-Power. | Watts per Candle. | Candle-Power. | Watts per Candle. |
|---|---|---|---|
| 10·5 | 4·10 | 10·5 | 4·04 |
| 11·9 | 3·77 | 8·4 | 4·10 |
| 7·37 | 5·41 | 9·73 | 4·23 |
| 7·65 | 4·51 | 10·05 | 4·19 |
| 12·68 | 3·43 | 9·78 | 4·31 |
| 11·25 | 3·92 | | |

In these lamps, as in the others we tested, the blackening of the bulbs was very slight indeed. Since the above measurements were made, the two lamps whose candle-powers were 11·9 and 11·25 have broken after about another hundred hours of life without, as far as could be judged, any diminution in their light or any increase in the blackening of their bulbs.

Moreover, although the rise of candle-power seen in figs. 10 and 10 *a* was always accompanied with a rise in current, yet, as the rise in candle-power was proportionally much greater than the rise in current for the lamps we tested, as will be seen from figs. 10 and 10 *a*, where one division represents 50 per cent. change in the light, but only 4 per cent. change in the current, the consumption of power per candle was actually *less* after the lamp had run for 50 hours than it was at the beginning, and the power per candle did not rise seriously during the whole life of a lamp.

Examining the results for the group run at 100 volts, we see that in the first 124 hours the candle-power rose from 26·3 to 35, or by 33·1 per cent., the current in the same time rising from 1·261 to 1·335 amperes, or by 5·87 per cent., so that during these first hours the watts per candle dropped from 4·79 to 3·82.

During the 1820 hours of running, three lamps broke in this group, their lives being 572, 957, and 1167 hours; the three still unbroken at the end of the tests had been run for 1248, 863, and 653 hours respectively.

Over the first 500 hours the average consumption of energy with the lamps run at 100 volts was at the rate of 4·0 watts per candle, over the second 500 hours 4·36 watts per candle, over the third 500 hours 4·55 watts per candle, and over the whole run the average efficiency was 0·23 candle per watt, corresponding with 4·35 watts per candle.

The candle-power of the three lamps run at 101 volts rose in the first 150 hours from 26·5 to 30·6, that is by 15·5 per cent., the current rose from 1·27 to 1·33, or by 4·72 per cent., the watts per candle in the same time falling from 4·80 to 4·32. The average watts per candle over the whole run of 1340 hours of this group were 4·68, corresponding with an efficiency of 0·215 candle per watt.

In the group at 102 volts which was run for 1820 hours six lamps broke, their lives being 242, 372, 516, 570, 516, and 786 hours respectively in the order of breaking; the three lamps unbroken at the end of the tests had run for 1148, 898, and 772 hours respectively.

The initial rise in candle-power in this group at 102 volts was from 30·6 to 35, or a rise in 120 hours of 14·4 per cent., the current in the same time rose from 1·26 to 1·31 amperes, or by 3·97 per cent., so that the watts per candle diminished from 4·22 to 3·82.

The average consumption of energy during the first 500 hours was at the rate of 3·9 watts per candle, during the second 500 hours 4·06 watts per candle, during the third 500 hours 4·2 watts per candle, and over the whole run the average was 4·12 watts per candle, corresponding with an efficiency of 0·243 candle per watt.

Turning to the group run at 104 volts, the curves show that the breakages were very frequent. Altogether five lamps broke, their lives being 94, 175, 210, 242, and 254 hours; the three lamps left unbroken at the end of the test had been run for 165, 222, and 364 hours.

The initial rise in candle-power was from 33·8 to 40·5 candles, that is 19·8 per cent.; and the current rose from 1·264 to 1·307 amperes, or by 3·4 per cent.

Over the whole run the average watts per candle, for the lamps run at 104 volts, were 3·6, corresponding with an efficiency of 0·278 candle per watt.

It is known from preceding tests (see the 'Electrician,' July 15th, 1892, for example) that the light given out by a new glow-lamp varies approximately as the seventh power of the pressure when the pressure is something like the normal pressure for the lamp. Now, as the groups of lamps that we tested at 100, 102, and 104 volts respectively were selected so that each group gave practically the same light initially when tested at the same pressure of 100 volts, it was to be expected that the three groups run at the three different pressures would follow the law for the light given out by the same lamp when used at different pressures.

And this is practically the case, for if $L_{100}$, $L_{102}$, and $L_{104}$ be the number of candles emitted by the three groups of three lamps each, we see from the curves on fig. 10 that at the start

$$L_{100}=26·3,\ L_{102}=30·6,\ L_{104}=32·5\ ;$$

$$\therefore\ \frac{L_{102}}{L_{100}}=1·16,\ \text{and}\ \frac{L_{104}}{L_{100}}=1·24.$$

Hence the light is roughly as the seventh power of the pressure at the start.

But after the lamps have been glowing for 100 hours this relationship no longer holds, for after 100 hours from the start we see from the curves on fig. 10 that

$$L_{100}=33·9,\ L_{102}=34·1,\ L_{104}=39·8,$$

or $$\frac{L_{102}}{L_{100}}=1,\quad \frac{L_{104}}{L_{100}}=1·17,$$

so that the light varies only as something like the fourth power of the pressure.

On the other hand, if we consider the results of the preliminary tests recorded in fig. 10*a*, we have at the start

$$L_{100}=24·8,\quad L_{102}=28·7,\quad L_{104}=30,$$

so that

$$\frac{L_{102}}{L_{100}}=1·16,\quad \frac{L_{104}}{L_{100}}=1·21\ ;$$

while after 100 hours' run

$$L_{100} = 33\cdot 1, \quad L_{102} = 38, \quad L_{104} = 43\cdot 3;$$

so that

$$\frac{L_{102}}{L_{100}} = 1\cdot 15, \quad \frac{L_{104}}{L_{100}} = 1\cdot 31.$$

In this case, then, the law of the seventh power holds roughly not only for the light given out by the three groups at the start but also at the end of the first 100 hours' run.

The following table gives the analysis of the chief results shown by the curves on figs. 10 and 10 *a*.

| | Preliminary Tests. | | | Later Tests. | | | |
|---|---|---|---|---|---|---|---|
| Pressure in Volts maintained between Lamp Terminals ............... | 100 | 102 | 104 | 100 | 101 | 102 | 104 |
| Duration of Test, in Hours | 110 | 110 | 110 | 1,820 | 1,340 | 1,820 | 460 |
| Initial Candle-Power per Lamp .................. | 8·23 | 9·57 | 10 | 8·77 | 8·83 | 10·2 | 11·27 |
| Initial Watts per Candle... | 4·72 | 4·37 | 4·20 | 4·79 | 4·80 | 4·22 | 3·89 |
| Largest Candle-Power per Lamp .............. | 11·1 | 12·6 | 14·5 | 11·67 | 10·23 | 11·67 | 13·5 |
| Percentage Rise in Candle-Power at the beginning .................. | 35·0 | 31·9 | 45·0 | 33·1 | 15·5 | 14·4 | 19·8 |
| Percentage Rise in Current at the beginning | 7·55 | 4·87 | 7·43 | 5·87 | 4·28 | 3·97 | 3·4 |
| Smallest Watts per Candle .................. | 3·74 | 3·48 | 3·12 | 3·82 | 4·3 | 3·82 | 3·33 |
| Average Candle-Power per Lamp during whole run ......................... | ... | ... | ... | 10·0 | 9·4 | 10·7 | 12·1 |
| Average Watts per Candle during whole run | ... | ... | ... | 4·35 | 4·68 | 4·12 | 3·6 |
| Lives in Hours of Lamps Broken during run ... | ... | ... | ... | 572; 957; 1167. | No Lamps broken. | 242; 372; 516; 540; 516; 786. | 94; 175; 210; 242; 254. |
| Lives in Hours of Unbroken Lamps ......... | ... | ... | ... | 1248; 863; 653. | 1340; 1340; 1340. | 1148; 898; 772. | 165; 222; 364. |
| Number of Lamps included in Striking Averages .............. | ... | ... | ... | 6 | 3 | 9 | 8 |

Although, as already stated, the number of lamps that could be supplied with power every night at the Central Technical College was limited to nine, and although, therefore, the total number dealt with in the investigation was small, the curves on figs. 10 and 10*a*, and the results given in the preceding table, are quite sufficient to enable us to arrive at the following results :—

(1) When a group of Edison-Swan lamps marked 100–8 are run at 100 volts, and each lamp, as its filament breaks, is replaced by a *new* Edison-Swan 100–8 lamp, it may be expected that the light given out by the group will never be as small as it was at the beginning, when all the lamps in the group were new. This important result is brought about by the deterioration of the lamps with long-lived filaments being compensated by the great rise in the light given out by each new lamp when put in place of one whose filament has broken.

(2) An Edison-Swan lamp marked 100–8 when run at 100 volts will give an average illumination during its whole life of about 10 candles, and will absorb an average power of about 4·3 watts per candle, so that such a lamp must be regarded as a 43-watt lamp, and not a 30-watt lamp as is not unfrequently stated, this difference in power being about 43 per cent.

(3) An Edison-Swan lamp marked 100–8 may, when run at 100 volts, emit during a large portion of its life a light of as much as 11·7 candles, and absorb a power of about 44·6 watts, which is about 44 per cent. greater than the nominal 30 watts.

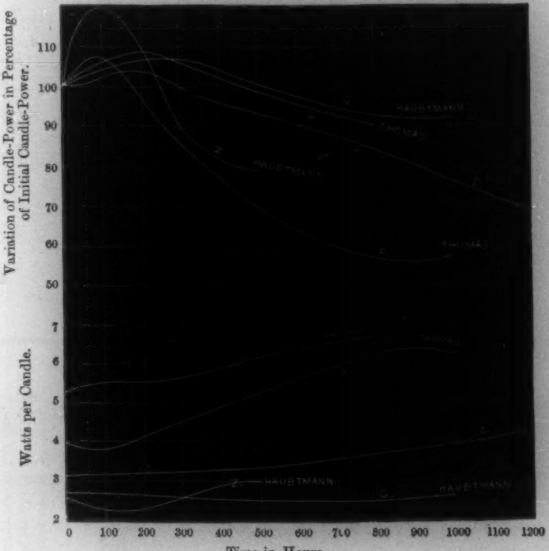
These last two facts are of great importance to dynamo-constructors, when specifying, as is frequently done, the number of lamps of a given type to which a given dynamo can supply current to without becoming too hot. For if, in making such a calculation, it be assumed that an Edison-Swan 8-candle-power lamp absorbs the nominal 30 watts, that is 3·75 watts a candle instead of the 44·6 watts which our tests show that such a lamp actually absorbs during a long portion of its life, the current will be 44 per cent. greater, and the rate of heating of the dynamo 108 per cent. greater, than was anticipated.

(4) Groups of new Edison-Swan lamps marked 100–8, if selected so as to give the same light at 100 volts, will, *when new*, emit a light which is roughly proportional to the seventh power of the pressure applied to them.

But after a run of 100 hours, this rule connecting light and pressure may, or may not, hold.

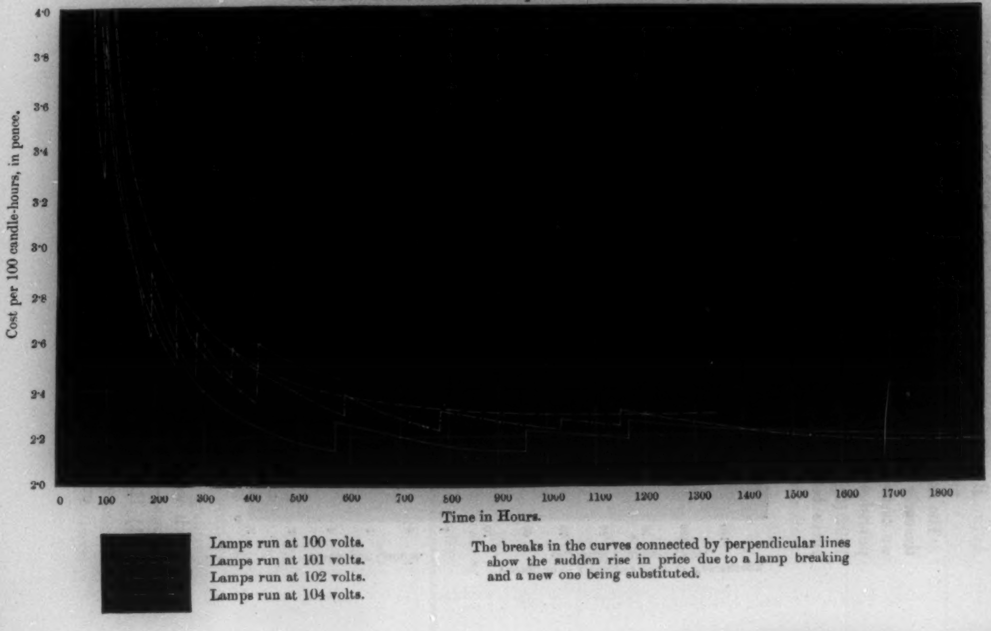
The rise in candle-power with time, which occurred during the early part of the life of all the Edison-Swan lamps which we tested, may be noticed also in the collection of curves published by Mr. Feldman in the 'Electrician,' Nov. 29th, 1892 (fig. 11). But there are certain very important differences between the results recorded by these curves and those which we have obtained. These differences are shortly as follows:—

Fig. 11.



(1) The greatest rise of light emitted by the lamps as recorded in Mr. Feldman's curves was 14 per cent. In our experiments this maximum rise was 45 per cent.

Fig. 12.—Life Tests on Edison-Swan 8 C.P. 100-volt Lamps. Curves showing the relation between Cost of Light and Time. Price of a Board of Trade unit 4½*d*. Cost of a new lamp 1*s*. 9*d*.



The breaks in the curves connected by perpendicular lines show the sudden rise in price due to a lamp breaking and a new one being substituted.

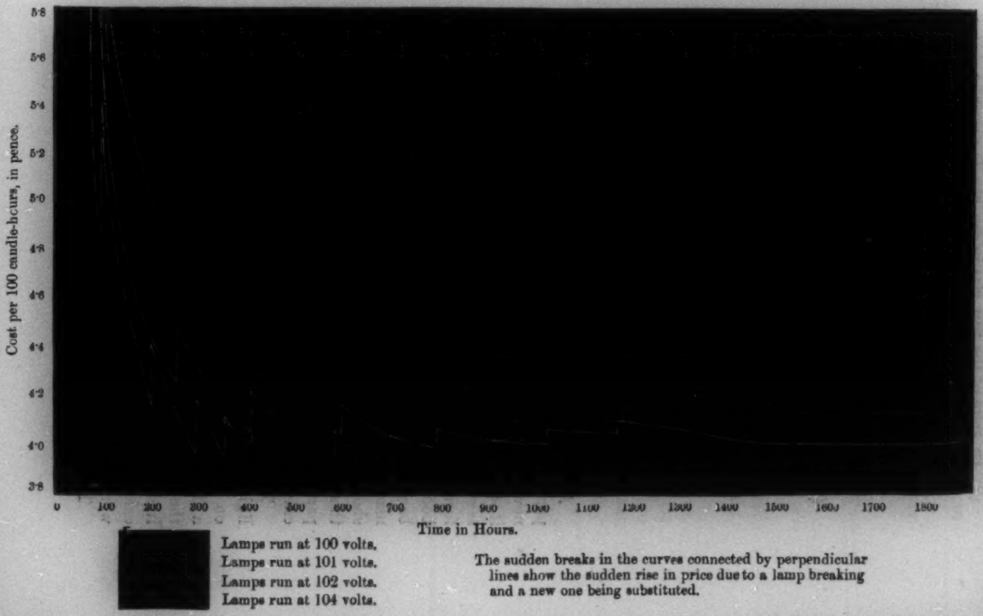


Fig. 13.—Life Tests on Edison-Swan 8 C.P. 100-volt Lamps. Curves showing the relation between Cost of Light and Time. Price of a Board of Trade unit 9*d.* Cost of a new lamp 1*s.* 9*d.*

The sudden breaks in the curves connected by perpendicular lines show the sudden rise in price due to a lamp breaking and a new one being substituted.

(2) In spite of the first rise in the candle-power as shown in Mr. Feldman's curves (fig. 11), the candle-power at the end of the life of the lamps was in all cases much less than it was when the lamps were new. Whereas with the lamps which we tested at 100, 101, and 102 volts the light given out by a group was never as low as it was at the beginning when the lamps were new.

(3) In spite of the first rise in candle-power recorded in the curves on fig. 11, it was only for the lamps whose behaviour was recorded in curves P and Z that the power expended per candle diminished at first with time. And even in the case of these two sets the power expended per candle increased again, and was greater when the filaments broke than it was when the lamps were new. Whereas in our tests the power expended per candle not only diminished considerably during the early life of the lamp, but it never rose again as high as it was when the lamps were new.

Although, then, the rise in candle-power during the early part of the life of a glow-lamp is apparently not an absolutely new fact, the magnitude of the rise and the effects resulting from it were, in the older lamps, so trifling that no special attention seems to have been devoted to this important subject in the former reports of tests of lamps. Indeed, even in a prominent book connected with glow-lamps which has quite recently been brought out in this country, no mention whatever is made of the fact in question. And yet, as we have already shown, and as will become more apparent from what follows, this remarkable rise in the candle-power during the earlier part of the life of an Edison-Swan lamp has a very important effect on the economy of lighting with glow-lamps.

The next point toconsider is the way in which the cost of lighting with the modern 100–8 Edison-Swan lamps depends on the pressure at which they are run, and on the cost of a Board of Trade unit. The curves on figs. 12 and 13 give the cost of obtaining light with the various groups of lamps, including the cost of replacing lamps with broken filaments, calculated day by day from our tests as the experiment went on.

The ordinates of the curves show the cost of 100 candle-hours at any time during the test, time being measured horizontally, and the values of the ordinates have been calculated from the following formula:—

Total cost per candle per 100 hours at the end of any number of hours $t$ equals

$$100 \times \frac{\text{Board of Trade units used during time } t \times \text{Price of one Board of Trade unit}}{\text{Total Candle-hours during time } t}$$

$$+100 \times \frac{\text{Number of lamps used during time } t \times \text{Price of one lamp}}{\text{Total Candle-hours during time } t}.$$

The price of a kilowatt-hour we took as 4½*d* in fig. 12, and as 9*d*. in fig. 13, the cost of a new lamp being taken as 1*s*. 9*d*. in both sets of curves.

Of course, it will be seen from the formula quoted above, that whenever a lamp breaks and a new one is put in its place, there must be a sudden, though temporary, rise in the cost per candle-hour due to the cost of the new lamp; but this rise becomes less marked as the number of lamps included in the calculations increases, and would have become inappreciable if the tests could have been carried on for a sufficient length of time.

The first three lamps to break in both the 102 and the 104 volt groups were replaced by the lamps which we had previously run at 102 and 104 volts respectively for 110 hours; and in calculating the cost-curves we have added in the watt-hours and the candle-hours due to these previous runs; we have also added to the abscissæ of the curves the 110 hours.

On examining the total-cost curves on figs. 12 and 13, it is at once apparent that they nowhere show any such rise in the cost of producing light, as was seen in the similar curves for American lamps (fig. 5). The curves in fig. 12, for which the price of a Board-of-Trade unit was taken as 4½*d*., do *not* turn up *at any* point, not even for the three lamps run at 101 volts, which lasted unbroken for over 1300 hours.

In fig. 13, however, for drawing the curves on which the price of a Board-of-Trade unit has been taken at 9*d*., there are slight indications of the curves turning up: for example, the curve for the 100-volt group rises a little at 850 hours, at which time the lives of the three lamps being tested were 850, 850, and 278 hours; and, again, at about 1600 hours, when the lives of the three living lamps were 1028, 643, and 433 hours, the cost per candle-hour rises a little. In the group run at 101 volts the cost of lighting began to rise a little after the lamps had been lit for 1100 hours; and in the 102-volt group the curve (fig. 13) turns up a little at 1700 hours, at which time the ages of the lamps alight were 928, 678, and 552 hours. But at no one of these points is there a sufficient rise to indicate that a time has been reached when it would be good economy to discard lamps.

The remaining total cost curve on fig. 13, viz. that for the group of lamps run at 104 volts, when the price of the Board of Trade unit is taken at 9*d*., does not show any indication of a minimum point.

Hence, generally, we may conclude that when the modern Edison-Swan 8 C.P. 100-volt lamps such as we have been testing, costing 1*s*. 9*d*. per lamp, are supplied with energy costing 9*d*. per Board of Trade unit, no economy will be gained by discarding the lamps before the filaments break.

This important result is of course due to the fact, already pointed out, that there is no marked decrease in the candle-power of the lamps during their lives.

Owing to the extent to which the individual lamps varied among themselves, it is difficult to say which of the four pressures at which we tested lamps would be the most economical to use. The three lamps tested at 101 volts seem to have been quite abnormal, their efficiency being very low, and, as a consequence, their lives very long.

With a Board of Trade unit costing 4½*d*., the lamps tested at 100 volts gave the cheapest light, and as they do not seem to have been above the average in quality this result may probably be safely taken as correct.

With energy costing 9*d*. per Board of Trade unit (fig. 13) there does not seem much to choose between the total cost of producing light with the three pressures of 100, 102, and 104 volts, excepting that the use of 104 volts would introduce an extra expense arising from the labour of frequently replacing broken lamps.

The two conclusions, then, to which we are led by a study of these total-cost curves on figs. 12 and 13 are :—

1. The modern Edison-Swan 8 C.P. 100-volt lamps such as we tested should not be discarded until the filaments break.
2. No marked economy can be gained by over-running this type of lamp.

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*Addition made January* 25, 1895.

The question arises—what is the cause of the marked rise in candle-power which occurred with all the lamps tested by us during 1893 and 1894? In the early summer of 1894, when our tests were approaching completion, Mr. Howell, in contributing to a discussion at the American Institute of Electrical Engineers, stated that such a rise in candle-power was due to the vacuum of the lamp improving during the early part of its life. Therefore, after we had stopped the main investigation, we made some experiments to test the validity of Mr. Howell's explanation.

We applied the induction-coil vacuum-test to some dozen Edison-Swan lamps when quite new, and again after they had been run for about 80 hours at their normal pressure of 100 volts. In *every case* we found that the vacuum had apparently improved; for using a spark of about 8 millimetres in length, the lamps when *new* were entirely filled with a bright blue glow accompanied with some bright white patches on the glass; whereas, after a run of about 80 hours at a pressure of 100 volts, this phosphorescent effect with the 8 millimetre spark was either entirely absent, or consisted of only a faint nebulous glow which did *not* fill the lamp-bulb, and there was very little light on the surface of the glass.

Thus it appeared as if Mr. Howell's explanation of the great increase in the light given out by a glow-lamp during the early portion of its life was correct.

But this conclusion which we arrived at last year has been modified by tests that we have been carrying out on Edison-Swan glow-lamps purchased since our paper was sent in to the Physical Society in November 1894. For we find that,—while the induction-coil vacuum-test applied to these lamps when they are new, and after a run of 80 hours at the normal pressure of 100 volts, shows that the vacuum apparently improves,—this improvement in the vacuum is not accompanied with the great rise in candle-power which we found with all the Edison-Swan lamps purchased in 1892 and 1893, the tests of which form the subject of this paper. And yet the lamps are all marked in the same way, "100 E.F. 8," and they all look alike.

In the case of a set of these Edison-Swan lamps, purchased on January 21, 1895, not merely were the current and the light periodically measured, but the induction-coil vacuum-test was applied at intervals during the 80 hours' run; and it was found that the change in the phosphorescent appearance of the lamp, and the consequent apparent increase in the vacuum, was produced slowly and not suddenly on the first application of the pressure of 100 volts.

The following are the results of the tests of this batch of six lamps. The light was measured with a Harcourt-Pentane Standard, the potential difference with the Ayrton and Mather reflecting electrostatic voltmeter, and the current with the strip of manganin shunted with the Ayrton and Mather moving coil-galvanometer; this voltmeter and the ammeter combination being the same as those employed with all the lamps tested previously. But both instruments were carefully calibrated on January of this year, to make quite certain that the different behaviour of these newer lamps was not merely an apparent one produced by some change having occurred in the sensibilities of the measuring-instruments.

The insulation of the lamp-holders was carefully cleaned and the contact-surfaces scraped before these tests were made.

From these tests it is seen that, in the case of lamps Nos. XI. and XIV., there was practically no change either in the light or in the power absorbed during the first 80 hours of the running at the constant pressure of 100 volts; and that in the case of the remainder of this batch of lamps the increase in the light and in the power absorbed was comparatively small, the greatest change being with lamp No. XII., where the light rose by about 11 per cent. and the power by about 4 per cent. This is a very different result from that obtained with the Edison-Swan lamps previously tested, and run at a constant pressure of 100 volts, for there the total

Six Edison-Swan Lamps, marked "100 E.F. 8," purchased January 21, 1895, marked by us IX., X., XI., XII., XIII., XIV., and run at 100 Volts.

Filaments placed at an angle of 45° with the Photometer-Bench.

| Hours of Running. | Power, in Watts. | Candle-Power. | Watts per Candle. |
|---|---|---|---|
| Lamp No. IX. | | | |
| 0 | 41·3 | 9·70 | 4·26 |
| 1 hour 40 minutes. | 41·3 | 9·70 | 4·26 |
| 6 hours 10 minutes. | 41·5 | 9·70 | 4·28 |
| 13 hours 30 minutes. | 41·6 | 9·67 | 4·30 |
| 42 hours 30 minutes. | 41·9 | 9·85 | 4·25 |
| 80 hours ..... ......... | 42·5 | 9·85 | 4·31 |
| Lamp No. X. | | | |
| 0 | 40·35 | 7·85 | 5·14 |
| 1 hour 45 minutes. | 40·4 | 7·95 | 5·08 |
| 6 hours 15 minutes. | 40·5 | 7·92 | 5·11 |
| 13 hours 35 minutes. | 40·6 | 7·92 | 5·12 |
| 42 hours 35 minutes. | 40·9 | 8·2 | 4·99 |
| 80 hours 5 minutes. | 41·5 | 8·5 | 4·88 |
| Lamp No. XI. | | | |
| 0 | 39·8 | 7·89 | 5·05 |
| 1 hour 50 minutes. | 39·8 | 8·00 | 4·97 |
| 6 hours 20 minutes. | 39·8 | 8·11 | 4·91 |
| 13 hours 40 minutes. | 39·8 | 7·95 | 5·01 |
| 42 hours 40 minutes. | 39·8 | 8·00 | 4·97 |
| 80 hours 10 minutes. | 40·1 | 8·00 | 5·01 |
| Lamp No. XII. | | | |
| 0 | 39·85 | 7·78 | 5·12 |
| 1 hour 55 minutes. | 40·1 | 8·07 | 4·97 |
| 6 hours 25 minutes. | 40·25 | 8·05 | 5·00 |
| 13 hours 45 minutes. | 40·41 | 7·95 | 5·08 |
| 42 hours 45 minutes. | 40·75 | 8·3 | 4·91 |
| 80 hours 15 minutes. | 41·4 | 8·7 | 4·76 |
| Lamp No. XIII. | | | |
| 0 | 40·75 | 8·06 | 5·05 |
| 2 hours ............... | 40·6 | 8·06 | 5·04 |
| 6 hours 30 minutes. | 40·5 | 8·17 | 4·95 |
| 13 hours 50 minutes. | 40·5 | 7·85 | 5·15 |
| 42 hours 50 minutes. | 40·5 | 7·9 | 5·13 |
| 80 hours 20 minutes. | 40·6 | 8·4 | 4·67 |
| Lamp No. XIV. | | | |
| 0 | 41·2 | 8·49 | 4·85 |
| 2 hours 5 minutes. | 41·2 | 8·65 | 4·76 |
| 6 hours 35 minutes. | 41·2 | 8·65 | 4·76 |
| 13 hours 55 minutes. | 41·2 | 8·49 | 4·85 |
| 42 hours 55 minutes. | 41·2 | 8·6 | 4·80 |
| 80 hours 25 minutes. | 41·5 | 8·5 | 4·89 |

light given out by the three lamps together rose by 35 per cent. in the first 100 hours of running, and the power by 7·55 per cent.

Since, then, as already stated, the vacuum, when tested periodically with the induction-coil, appeared to improve steadily with each of the six lamps Nos. IX. to XIV. during the run of 80 hours, it would appear that improvement in the vacuum was *not* the sole cause, as stated by Mr. Howell, for the great rise in the candle-power such as we observed with all the Edison-Swan lamps which we tested in 1893 and 1894.

It is possible that this rise in candle-power may have been due to a change in the surface of the filament causing the emissivity for heat to decrease, since that would raise the light emitted, as well as the number of candles per watt. Whether such a change in the heat-emissivity of the filament occurs with time we have not yet found out.

Another point of difference between this batch of six lamps Nos. IX. to XIV. and those which we tested during the main part of our investigation, is the relative inefficiency of these six lamps. For in no single test at any time during the 80 hours run with these six lamps were the watts per candle less than 4·25, and in many cases they were over 5; while with lamp No. XIII. the watts per candle, as seen in the last table, were as high as 5·15 after this lamp had been run for 13 hours 50 minutes. It is possible, then, that when in the body of the paper we spoke of the group of three lamps which we ran at a constant pressure of 101 volts as being "quite abnormal," because the average watts per candle required with this group during the run of 1340 hours were as high as 4·68, we ought rather to have spoken of the various other groups of lamps which we ran at the constant pressures of 100, 102, and 104 volts respectively as being abnormally good Edison-Swan lamps.

At any rate it is clear that it is at present impossible to state the most economical potential difference to employ with any Edison-Swan lamps marked "100 E.F. 8;" since batches of lamps so marked, and therefore nominally the same, really require very different potential differences to be employed to obtain maximum economy with a given price of lamp and of a kilowatt-hour.

It may, however, be concluded, from the curves shown in figs. 12 and 13, that the most economical potential difference to employ with any Edison-Swan lamps marked "100 E.F. 8," such as have been obtainable in the open market since 1892, is the potential difference that will cause the lamp during a large portion of its life to have an efficiency of about 0·25 candle per watt, corresponding with 4 watts per candle.

The value of this potential difference for any batch of these lamps may be determined approximately in the following way. From our tests, already referred to, of eleven Edison-Swan lamps, marked "100 E.F. 8," which had been used in a house for some 200 or 300 hours, we found that the relation between candle-power and pressure was given by

$$\text{Candle-power} = a \times (\text{volts})^{5{\cdot}91},$$

where $a$ is a constant. Also we found that the relation between candle-power and watts for these lamps was given by

$$\text{Candle-power} = b \times (\text{watts})^{2{\cdot}9},$$

where $b$ is a constant. Therefore

$$\text{Volts} = c \times (\text{watts per candle})^{-0{\cdot}258},$$

where $c$ is a constant.

Hence if one has a batch of Edison-Swan lamps marked "100 E.F. 8," whose efficiency is, say, 0·222 candle per watt, corresponding with 4·5 watts per candle, when a pressure of 100 volts is applied to them, it would be probably most economical to run them at about 103 volts, since this is the pressure which the last equation tells us will be necessary to raise the efficiency of such lamps to 0·25 candle per watt.

From what precedes, it follows that, since the average efficiency of the 100 E.F. 8 Edison-Swan appears to be less than 0·25 candle per watt, the opinion expressed by one of us in an article entitled "New Lamps for Old," published in the 'Electrician' for September 29, 1893, was correct, viz. that it would be economical to overrun Edison-Swan lamps by applying a pressure about 3 per cent. higher than the marked pressure. And that the reason why this conclusion was apparently negatived by the results of the tests which we carried out during the winter of 1893 and a large portion of

1894, was because the various groups of lamps which we ran at the constant pressures of 100, 102, and 104 volts respectively consisted of specially good specimens.

In applying the rule that the economical potential difference is about the one which causes the lamp to produce 0·25 candle per watt, it is important, however, to examine 8-candle 100-volt Edison-Swan lamps when bought to see whether they are really marked "100 E.F. 8." For while the result of various purchases of 8-candle 100-volt Edison-Swan lamps during the past three years has always resulted in lamps marked "100 E.F. 8" being sent us, although the marking on the lamps was never specified by us, a recent batch of lamps that we have received contained among them certain lamps marked "100 B. 8," which not only differed in the marking but also in the filament being of a simple horse-shoe shape, and not with a loop at the top as in the case of the other lamps. And, on testing these Edison-Swan B lamps, we were surprised to find that with no one of them, when run at 100 volts, did the watts per candle exceed 3·9, and in some cases the watts per candle were as low as 3·01. We have not, however, had these B lamps for a sufficiently long time in our possession to be able to express any opinion about their life-history.

## DISCUSSION.

Professor RÜCKER asked if it made any difference to the life of a lamp whether it were kept running continuously until the fibre broke, or were run for periods of a few hours, alternating with intervals of rest. The latter case would more nearly correspond with the conditions obtaining in practice.

Professor AYRTON replied that the lamps were kept running during the night, and were disconnected during the day.

## XXXIX. *The Tin-Chromic Chloride Cell.*

### *By* S. SKINNER, *M.A.*[*]

A CELL consisting of a tin and platinum couple in a solution of the green chromic chloride was described by W. E. Case in the Proc. R. S. 1886, p. 345. The tin is dissolved by the chromic chloride at a high temperature only, and when the solution is cooled the tin is precipitated. The chemical changes are represented by the following statement:—

$$Cr_2Cl_6 + Sn \rightleftharpoons SnCl_2 + 2CrCl_2.$$

As the reaction is reversed on cooling, the cell has the interesting feature that at the end of a hot and cold cycle it is in the same chemical condition as it was at the commencement. It thus offers a method of deriving electrical energy directly from heat. The author of the account gives a curve of electromotive force, and finds that it is zero at 60° F., and increases to about $\frac{1}{4}$ volt at 200° F. I shall show that the E.M.F. is not zero at the ordinary temperature, but is about $\frac{1}{2}$ volt; however, the cell will not give any current at these temperatures on account of polarization. It appears that the curve given by Mr. Case is not an E.M.F. curve, but one which was probably obtained by using a wire voltmeter, and therefore really represents the current the cell is capable of producing.

The tin is precipitated in small crystals from the cooling solution of $CrCl_2$ and $SnCl_2$, and does not then form a satisfactory electrode. I have therefore arranged the cell with an amalgam of tin in place of the solid rod. The precipitated crystals fall into the mercury and dissolve so as to reconstitute a suitable electrode. My construction of the cell is very much like that of a Clark cell.

A test-tube with a platinum wire through the base has fluid amalgam in it, and this is covered with a solution of pure $Cr_2Cl_6$, made by dissolving violet sublimed $Cr_2Cl_6$ in water with the aid of a fragment of tinfoil. A platinum plate and wire form the positive pole of the cell.

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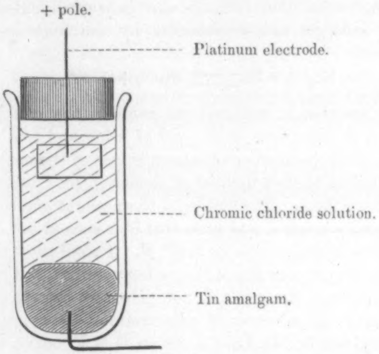
[*] Read February 8, 1895.

Connecting such a cell at 15° C. with a galvanometer, there is a sudden deflexion which very rapidly becomes less until some small steady value is reached. On warming the cell the deflexion increases until it is relatively large. These observations show that the cell cannot produce a continuous current of any magnitude at low temperatures, but at high temperatures it does.



If the E.M.F. of the cell be measured on a potentiometer, or by means of a ballistic galvanometer and condenser, by either of which methods the cell is not called on to produce a current, it is found that the E.M.F. at all temperatures is approximately ½ volt, and that the E.M.F. is slightly less at the boiling-point of water than at the ordinary temperature.

The explanation of the results is not difficult. The cell polarizes very rapidly at low temperatures, and the opposing E.M.F. of polarization increases so rapidly and so largely that almost at the moment of connexion the effective E.M.F. becomes zero. The cell behaves like a condenser which is connected to a battery through a very high resistance. Such a condenser would discharge itself when its plates were connected, but when they were isolated again it would slowly become charged by the battery through the high resistance.

At the high temperature the polarization is very largely reduced, and the cell will produce a continuous current.

Another interesting feature of the cell is that it may be used as the mechanism of a heat-engine for the production of work, and we can trace in it the complete cycle of Carnot. Let the cell be placed in a hot chamber, and work may be derived from it until all the $Cr_2Cl_6$ or the tin is used. Then let the cell be placed in a cold chamber, it will give up heat, and becomes restored to its original chemical condition.

Measurements of the electromotive force of two cells are given in the following tables. The first cell contained tin-amalgam, and the second cell contained a tin rod. Both cells had not been used for producing current within the 24 hours immediately preceding the measurements.

Cell No. 1. Tin-amalgam.

| Temperature. | E.M.F. |
|---|---|
| 15·5° C. | ·44 volt. |
| 20·5 | ·45 |
| 49·0 | ·43 |
| 75·0 | ·41 |
| 93·0 | ·40 |
| 96·0 | ·40 |
| 97·0 | ·40 |
| 20·0 | ·44 |

Cell No. 2. Tin rod.

| Temperature. | E.M.F. |
|---|---|
| 16° | ·52 volt. |
| 30° | ·52 |
| 97° | ·45 |

Connexion was made and a current allowed to flow for 1 minute, and then the cell was allowed to rest for 1 minute :

| | |
|---|---|
| 97° | ·08 volt. |

At end of second minute :

| | |
|---|---|
| 97° | ·11 volt. |

At end of third minute :

| | |
|---|---|
| 97° | ·11 volt. |

These results showed that the cell had polarized, and was only slowly recovering its electromotive force.

When a solution of the green chromic chloride at the ordinary temperature has silver nitrate added to it, only two-thirds of the chlorine is precipitated. This, according to the theory of ionisation, indicates that only two atoms out of three act as negative ions, the other atom apparently being part of the positive ion. On the other hand, if a solution of chromic chloride near 100° be treated with silver nitrate, the whole of the chlorine may be precipitated. This indicates that at the higher temperature all the chlorine atoms behave as negative ions.

Taking this into account, the Grotthus chain representing the action of the cell about 15° must be as follows :—

$$\mathrm{Pt} \mid \mathrm{ClCrCl_2} \mid \mathrm{ClCrCl_2} \mid \mathrm{ClCrCl_2} \mid \mathrm{Sn},$$

becoming, after connexion,

$$\mathrm{Pt,ClCr} \mid \mathrm{Cl_2ClCr} \mid \mathrm{Cl_2ClCr} \mid \mathrm{Cl_2Sn}.$$

This view of the action leaves the ion ClCr polarizing the cell. Now if a depolarizer acts so as to remove this ion, the cell will go on producing a current. The excess of chromic chloride might perform this function, forming with this ion chromous chloride :

$$\mathrm{CrCl} + \mathrm{CrCl_3} = 2\mathrm{CrCl_2}.$$

The behaviour of the cell shows that this does not take place readily.

A similar view of the action in the cell at about 100° indicates the presence of chromium ions as the polarizing agent. At this temperature there is not much polarization ; so that it appears the following chemical change takes place readily :

$$\mathrm{Cr} + 2\mathrm{CrCl_3} = 3\mathrm{CrCl_2}.$$

## DISCUSSION.

Prof. **RÜCKER** asked whether a change of polarization would explain the behaviour of the cell at different temperatures.

Prof. **CAREY FOSTER** asked whether the reversed chemical action on cooling from a high temperature were accompanied by a reversed E.M.F.

Mr. Skinner said no; the tin was precipitated throughout the solution, and not at the surface of the tin plate, so that no E.M.F. of the kind was to be expected.

Mr. Appleyard thought that Prof. Minchin had used tin chloride cells with two tin plates for electrodes, the cells only working when one plate was illuminated.

Mr. Trotter wished to know whether heating the cell supplied energy to it, or simply removed an obstacle in the form of polarization.

Mr. Skinner thought that heating acted by removing an obstacle.

Capt. Abney—And so doing work.

## XL. *Note on a Simple Graphic Illustration of the Determinantal Relation of Dynamics.* *By* G. H. Bryan[*].

In the whole range of theoretical dynamics there is probably no theorem which is so difficult to fully grasp as the determinantal relation connecting the multiple differential of the initial coordinates and momenta of a system with that of its final coordinates and momenta. This relation, which may almost be regarded as the keystone to the Kinetic Theory of Gases, is conveniently written in the Jacobian form

$$\frac{d(p_1', p_2', \ldots, q_1', q_2', \ldots)}{d(p_1, p_2, \ldots, q_1, q_2, \ldots)} = 1,$$

where $p_1, p_2, \ldots$ are the generalized momenta corresponding to the generalized coordinates $q_1, q_2, \ldots$, and unaccented and accented letters refer respectively to initial values and final values after a fixed interval of time $t$.

To my mind the difficulty of grasping this result arises from the want of simple graphical illustrations and verifications from first principles not involving the use of the Calculus. The following illustrative examples of its applications to systems with one degree of freedom have afforded me great assistance in understanding the theorem, and I trust that they may prove useful to others.

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[*] Read April 26, 1895.

Consider a particle moving in the straight line OX (fig. 1) under any law of force. Let M be the position of the particle at any instant, and let the velocity of the particle at this instant be represented by the ordinate MP drawn at right angles to OX. Then, since the momentum is proportional to the velocity, the coordinates OM, MP represent the coordinate and momentum of the particle at the given instant, and we may call P the representative point.

Now let four such particles of equal mass be projected simultaneously, having the initial coordinates $x$ and $x+\delta x$ and the initial velocities $v$ and $v+\delta v$. The representative points will form a small rectangle P Q R S of area $\delta x \,.\, \delta v$.

Let P′ Q′ R′ S′ be the corresponding representative points at any subsequent instant $t$.

Then the determinantal relation asserts that the area of the small parallelogram P′ Q′ R′ S′ is equal to that of the rectangle P Q R S.

[Instead of taking four particles we might suppose the points P, Q, R, S to refer to the *same* particle projected with different initial conditions and allowed to move for a fixed time-interval $t$.]

This property may be verified from first principles in the following simple cases :—

Case I. *Let the motion be uniformly accelerated.* Then from the equations

$$v' = v + ft, \qquad x' = x + vt + \tfrac{1}{2}ft^2,$$

and the corresponding equations obtained by substituting $x+\delta x$ for $x$ and $v+\delta v$ for $v$, it is easy to see (fig. 1) that the parallelogram P′Q′R′S′ has its base P′Q′ parallel to OX and equal to PQ or $\delta x$, and its altitude equal to PQ or $\delta v$ Therefore

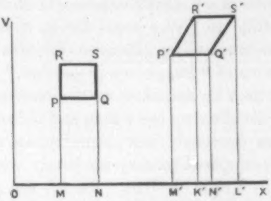
$$\text{area } \mathrm{P'Q'R'S'} = \text{area } \mathrm{PQRS}.$$

The parallelogram will, however, have undergone a shear, the points R, S having advanced beyond P, Q by an amount (M′K′=)$\delta v \,.\, t$. Hence

$$\cot \mathrm{RPQ} = t\,\frac{\delta v}{\delta x},$$

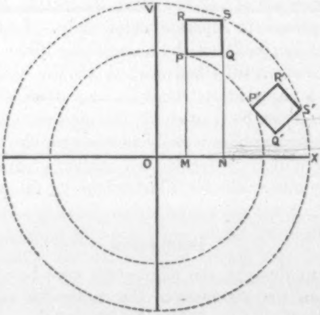
and is proportional to $t$. As the time increases, the diagonal P′S′ becomes more and more elongated, but the area of the parallelogram remains the same.

Fig. 1.



CASE II. *Let the motion be simple harmonic*, the acceleration varying as the distance from a fixed point O (fig. 2). Then, by properly choosing the scale of representation of velocity, the representative points of different particles will all describe concentric circles about O with uniform angular velocity. Hence the figure PQRS will be brought into the position P′Q′R′S′ by rotating about O through a certain angle, and the areas of the two figures will of course be equal.

Fig. 2.



Case I. might be deduced as the limit of Case II. by (i.) reducing the scale of representation of velocity so that the circles become projected into ellipses ; (ii.) supposing the centre O to go off to infinity, so that these ellipses gradually become elongated into parabolas.

The case of a repulsive force varying directly as the distance would be a little more complicated ; and it therefore seems hardly worth while to give a proof for it, though the legitimacy of the corresponding inference for this case might be inferred by means of "imaginary projection." The theorem might possibly then be extended to the case of any variable law of force by dividing up the times, and therefore the corresponding spaces decribed, into elements so small that the force might be supposed to vary uniformly with the distance along OX in any single element. This is not put forward as a satisfactory proof, but then the object of this note was to show, not how to prove the theorem, but how to convince oneself of its truth after proving it by highly analytical methods. This I found hard in the case of systems like that of Case I., where a slight variation in the initial conditions (viz. the difference of velocity $\delta v$ of the points M′K′) causes two such systems to separate indefinitely. I could not see how this was compatible with the multiple differential $(\delta x \,.\, \delta v)$ remaining constant till I had worked out the above explanation. It is a pity that systems with more than one degree of freedom could not be treated by this graphic method, but a similar objection applies equally to the graphic proof of the formula for uniformly accelerated motion of our text-books and to many other valuable illustrations of the principles of dynamics.

## Discussion.

Dr. Stoney thought the arguments were based on actions depending on the distances of the molecules and the supposition that they were rigid. In his opinion events occur in nature which are not represented by this simple theory, and great reservation should be shown in accepting dynamical problems which leave out of account actions occurring between matter and the ether. In nature nothing was large and nothing was small except relatively. Even molecules might possess infinite detail of structure. Their interaction with the ether must be considered in any complete theory.

# XLI. *On the Mechanical Analogue of Thermal Equilibrium between Bodies in Contact.* *By* G. H. BRYAN *and* LUDWIG BOLTZMANN[*].

[Abstract.]

THE great disadvantage of the Kinetic Theory has been that it has not hitherto furnished a very satisfactory proof of the fundamental property of temperature, namely, that two bodies in contact are at *equal temperature* when neither gains or loses heat from the other.

In a medium composed of two or more different kinds of gas molecules mixed together, the conditions of equilibrium of kinetic energy involve Avogadro's well-known law[†], namely, that the mean kinetic energies of translation of the different kinds of molecules shall be equal. From this we naturally infer that the quantity which represents *temperature* in the kinetic theory is proportional to the mean *vis viva* of translation. But our experimental knowledge of the properties of temperature is necessarily derived from observations of bodies which do *not* mix, and it is impossible to form a purely physical conception of the temperatures of two mixed gases apart from each other. We can only experiment on the temperature of the whole *mixture*.

It is therefore of great interest to devise a mechanical representation of the phenomena presented by two bodies between which transference of heat takes place by conduction, but whose molecules do not become indefinitely interdiffused. The system now to be described affords such a representation.

Let X and Y be two infinite parallel planes (or other surfaces) at a small distance apart, dividing space into three regions, $S_1$, $S_2$, and $\sigma$, of which the region $S_1$ lies to the left of X, the region $S_2$ lies to the right of Y, and the region $\sigma$ lies between the surfaces X, Y, and may be supposed to be very thin by supposing X, Y to be very near together.

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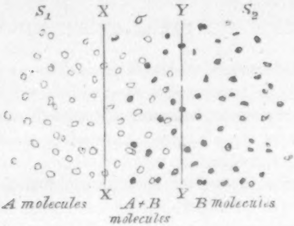
[*] This paper is taken from a memoir by Prof. Ludwig Boltzmann and G. H. Bryan, communicated by Prof. Boltzmann to the Imperial Academy of Vienna, Dec. 13, 1894. Read at the meeting of the Physical Society, April 26, 1895.

[†] *Wien. Sitzungsber.* vol. lxiii. 1871, vol. lxvi. 1872, vol. xciv. 1886, vol. xcv. 1887.



Let there be two different kinds of molecules A, B, the former represented in the figure by light, and the latter by dark points, and let these molecules be acted on by different laws of force specified as follows :—

(i) The plane Y shall be supposed to repel the A molecules with a force which vanishes at all points on the left-hand side of X, but which becomes infinitely great as we approach the plane Y itself so as to prevent any of the A molecules from crossing beyond Y and passing into the region $S_2$. This force shall not act on the B molecules.

(ii) In like manner, the plane X shall be supposed to repel the B molecules with a force which vanishes at all points on the right-hand side of Y, but which becomes infinitely great as we approach the plane X itself, so as to prevent any of the B molecules from crossing beyond X and passing into the region $S_1$. This force shall not act on any of the A molecules.

Then in the region $S_1$ we have a gas composed only of A molecules, and in the region $S_2$ we have a gas composed entirely of B molecules. Between these regions there is the region $\sigma$ containing a mixture of both kinds of molecules, and these molecules will collide with one another, and energy will thus be transferred from the molecules of one gas to those of the other.

The conditions of equilibrium of *vis viva* can be found by the usual methods, and the proof is applicable to the more general case where the A molecules are acted on by *any* external forces and the B molecules are acted on by any other external forces independent of the former forces, the two sets of molecules being mixed in those regions where the potentials of the two sets of forces are neither of them infinite. For this purpose it is convenient to use generalized coordinates.

Let $q_1, q_2, \ldots q_m$ be the generalized coordinates of an A molecule;

$p_1, p_2, \ldots p_m$, the corresponding generalized momenta;

$T_1$ its *vis viva*, $\chi_1$ its potential energy;

$E_1 = T_1 + \chi_1$ its total energy.

Also let $Q_1, Q_2, \ldots Q_n$ be the coordinates of a B molecule;

$P_1, P_2, \ldots P_n$ the corresponding momenta;

$T_2$ its *vis viva*, $\chi_2$ its potential energy;

$E_2 = T_2 + \chi_2$ its total energy.

Then, if $\chi_2$ is a different function of $Q_1, Q_2, \ldots Q_n$ to what $\chi_1$ is of $q_1, q_2, \ldots q_m$, the forces on the two kinds of molecules will be different.

Now it is proved* that if the number of A molecules whose coordinates and momenta be within the limits of the differential,

$$dp_1 \ldots . dp_m \, dq_1 \ldots . dq_m$$

is proportional to

$$Ae^{-h_1E_1} dp_1 \ldots . dp_m \, dq_1 \ldots . dq_m, \quad . \quad . \quad . \quad (1)$$

this distribution is permanent in the absence of collisions between the molecules, and is also unaffected by collisions between two A molecules.

Similarly if the B molecules are distributed with frequency proportional to

$$Be^{-h_2E_2} dP_1 \ldots . dP_n \, dQ_1 \ldots . dQ_n, \quad . \quad . \quad . \quad (2)$$

this distribution is stationary in the absence of collisions between the molecules, and is unaltered by collisions between two B molecules.

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* *Wien. Sitzungsber.* vol. lxxii. 1875, vol. lxxviii. 1878, vol. xcvi. 1887.

Lastly, we must consider the effect of collisions between an A molecule and a B molecule. Now if the time of duration of a collision is infinitely short, the coordinates of the colliding molecules are the same at the beginning and end of a collision. And if we consider only collisions between pairs of molecules which are in a given configuration so that the coordinates of the molecules have given values, the momenta of the colliding molecules will be distributed with frequencies respectively proportional to

$$A_1 e^{-h_1 T_1}\, dp_1 \ldots . dp_m,$$

and

$$B_1 e^{-h_2 T_2}\, dP_1 \ldots . dP_m,$$

where $A_1$ and $B_1$ are constants, the potential energies $\chi_1$ and $\chi_2$ being the same for all the molecules in the given configuration.

If, then, we write

$$f = A_1 e^{-h_1 T_1},\ F = B_1 e^{-h_2 T_2},$$

and if $f'$, $F'$ be the values of the corresponding quantities after the collision, it is proved by Dr. Boltzmann * that

$$fF = f'F' \, ; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and since finite forces have no effect during the infinitely small time of duration of a collision, the proof is independent of the finite forces between the molecules. The last equation gives

$$e^{-h_1 T_1 - h_2 T_2} = e^{-h_1 T_1' - h_2 T_2'},$$

that is

$$h_1 T_1 + h_2 T_2 = h_1 T_1' + h_2 T_2'.$$

But by the conservation of *vis viva*,

$$T_1 + T_2 = T_1' + T_2'.$$

Multiplying by $h_2$ and subtracting from the previous equation, we have

$$(h_1 - h_2)\, T_1 = (h_1 - h_2)\, T_1',$$

whence, since $T_1$, $T_1'$ are not in general equal,

$$h_1 - h_2 = 0, \text{ or } h_1 = h_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

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* *Wien. Sitzungsber.* vol. lxvi. 1872, last part.

The mean *vis viva's* of the A and B molecules are $3/2h_1$ and $3/2h_2$ and are therefore equal.

In my Report to the British Association I suggested that the distribution of a large number of molecules of the same or different kinds in which the coordinates ($q$) and momenta ($p$) are so arranged that the number of molecules in the neighbourhood of any given state is proportional to

$$e^{-hE} dp_1 \dots dp_n dq_1 \dots dq_n, \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

$h$ being the same for all kinds of molecules, be called *The Boltzmann-Maxwell Distribution*, the law which asserts the permanency of the Boltzmann-Maxwell distribution in any particular case being called *The Boltzmann-Maxwell Law*.

If these names be adopted, we have the result that the Boltzmann-Maxwell Law holds good for a mixture of different kinds of gas molecules, even when the forces which act on the molecules of one gas are entirely different from those which act on any other gas. The reasoning applies equally when there are any number of different kinds of molecules.

The densities of the A and B molecules are respectively proportional to

$$Me^{-h\chi_1} \text{ and } Ne^{-h\chi_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

where $M$ and $N$ are certain constants depending on the total numbers of respective molecules.

Hence if $\chi_1 = \infty$ over any region, that region contains only B molecules, and if $\chi_2 = \infty$ the region contains only A molecules, and the two kinds of molecules are mixed together in regions where $\chi_1$ and $\chi_2$ are both finite.

Instead of assuming a field of force of the kind considered above, we might assume the A molecules to be positively electrified and the B molecules to be negatively electrified, the planes X, Y being kept at a constant difference of potential. If this difference of potential be $V$ and if the charges on the respective molecules are $q_1 - q'$, the densities of the A molecules in the regions $S_1$ $S_2$ will be in the ratio of $1 : e^{-hqV}$, and the densities of the B molecules in the ratio of $e^{+hq'V} : 1$ and by making $V$ sufficiently great we shall make $e^{-hqV}$ and $e^{-hq'V'}$ very small, and the gases in the regions $S_1$, $S_2$ will be very nearly pure.

If collisions are replaced by encounters in which the molecules attract or repel one another with finite forces during a finite time, the same result may be proved by a method indicated by Prof. Boltzmann in his recent communication to the British Association, entitled "On the Application of the Determinantal Relation to the Kinetic Theory of Polyatomic Gases"*.

For the determinantal relation between the multiple differentials of the coordinates and momenta of a conservative dynamical system at the beginning and end of any interval of time $t'-t$ is of the form

$$\frac{\partial(p_1', \ldots p_m', q_1', \ldots q_m')}{\partial(p_1, \ldots p_m, q_1, \ldots q_m)}=1. \quad . \quad . \quad . \quad (6)$$

(1) If we apply this relation to a single molecule of gas moving about freely or in a field of external force, the relation will apply so long as the molecule considered does not encounter or collide with other molecules; and the possible laws of permanent distribution of the coordinates and momenta among a large number of such molecules may now be established thus:—

We know that for any one molecule the total energy is independent of the time or

$$E_1=\text{constant},$$

and the determinantal relation shows that the multiple differential

$$dp_1, \ldots . \, dp_m \, dq_1, \ldots . \, dq_m$$

is also independent of the time.

Therefore, if the law of distribution be such that the number of molecules included within the limits of the multiple differential at any instant of time ($t$) is

$$f_1(E_1)dp_1 \ldots . \, dq_m, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where $f_1$ denotes any function whatever, the same law will hold good at any subsequent instant of time ($t'$).

In particular, taking $f_1(E_1)=e^{-hE_1}$, we conclude that in the absence of such encounters any distribution determined by the expression (1) of the A molecules will be permanent, and a similar conclusion holds with respect to the distribution (2) of the B molecules.

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* Oxford Report, p. 102.

(2) We may take as our dynamical "system" a pair of molecules of the same or different kinds in the course of a binary encounter, it being assumed that the intermolecular forces remain finite during encounter, and that at each instant there are sufficient encounters of the same kind to give rise to a law of permanent distribution among the encountering sets of molecules. Here the multiple differential will have to include all the coordinates and momenta of all the molecules in the group considered. Hence if $E$ is the total energy of a pair of A and B molecules in the course of an encounter, any distribution of the pairs of molecules of the form

$$f(E)dp_1 \ldots dp_m\, dq_1 \ldots dq_m\, dP_1 \ldots dP_n\, dQ_1 \ldots dQ_n$$

will be permanent so long as the molecules of any one pair do not encounter any molecules not in that pair.

But in a gas each molecule will encounter various molecules in succession, so that the same pair of molecules cannot be considered permanently as a system apart from the rest. From this we find at once that if the frequency of distribution $f$ is a function of energy alone, it *must* be of the well-known form

$$f=e^{-hE}.$$

For *before* two molecules encounter each other, the frequency of distribution of the coordinates and momenta of one cannot depend on the coordinates and momenta of the other. Hence if $f_1$, $f_2$ denote the frequencies of distribution of the two molecules just before the encounter,

$$f_1 \times f_2 = f(E).$$

Now we may write

$$E = T_1 + T_2 + \chi_1 + \chi_2 + \chi_{12},$$

where $T_1$ $T_2$ are the kinetic energies of the two molecules, $\chi_1$ $\chi_2$ are the potential energies of the molecules due to the field of force, $\chi_{12}$ their mutual potential energy during the encounter.

But the same law must hold just before the encounter as during it, and just before the encounter $\chi_{12}$ is zero, so that

$$E = E_1 + E_2,$$

where $E_1$ $E_2$ are the separate energies of the molecules; and the resulting relation

$$f_1 \times f_2 = f(E_1 + E_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

can only be satisfied by

$$f_1 = e^{-hE_1}, \; f_2 = e^{-hE_2}, \; f = e^{-hE}.$$

Hence before and after the encounter the molecules have their coordinates and momenta distributed with frequencies proportional to $e^{-hE_1}$ and $e^{-hE_2}$ respectively. But *during* an encounter the frequency of distribution of *all* the coordinates and momenta of the pair or group is proportional to $e^{-hE}$, and the two encountering molecules cannot be considered separately.

For a pair of molecules we may write the function

$$\begin{aligned} f &= e^{-h(T_1+\chi_1+T_2+\chi_2+\chi_{12})} \\ &= e^{-hT} \times e^{-hT_2} \times e^{-h(\chi_1+\chi_2+\chi_{12})} \quad . \quad . \quad . \quad . \quad (9) \end{aligned}$$

This shows that for any given *configuration* the *momenta* of the molecules denoted by the suffixes 1, 2 are separately distributed with frequencies proportional to $e^{-hT_1}$ and $e^{-hT_2}$ respectively. The distribution of the *coordinates* of one molecule is not, however, independent of the position of the other owing to the presence of the factor $e^{-h\chi_{12}}$. When the encounter is over $\chi_{12}$ vanishes, this factor disappears, and the distributions of the coordinates of the two molecules become independent of each other, being of the forms (1) (2).

And since $\chi_1$ and $\chi_2$ may be of any forms whatever, and may be entirely different, the reasoning is immediately applicable to systems such as that which forms the subject of the present paper. Wherever $\chi_1$ or $\chi_2$ becomes infinite the number of molecules becomes zero, so that encounters do not there occur.

Similar reasoning holds good for encounters between two A molecules or between two B molecules or for simultaneous encounters between any number of molecules, provided that the encounters considered are sufficiently frequent to *have* a law of distribution.

And of course collisions can be treated as a limiting case of encounters.

The above brief investigation shows the advantage of applying the determinantal relation to encounters as well as to the free motion of molecules between encounters. With this method it is not necessary to start as Prof. Boltzmann previously did, by *assuming* the frequency of distribution to be determined by a function $f$ of the form $e^{-hE}$, but if we merely assume $f$ to be any function of the energy we may deduce that the form $f(E)=e^{-hE}$ is *necessary* as well as *sufficient*.

## XLII. *Note on a Neglected Experiment of* Ampère.

### *By* SILVANUS P. THOMPSON[*].

IN the year 1822 Ampère, being at Geneva, showed to De la Rive in his laboratory a number of his now classical experiments on the actions of conductors carrying currents upon other conductors and upon magnets. These are recounted by A. De la Rive in the *Annales de Chimie et de Physique*, xxi. p. 24 (1822).

Amongst these experiments there is one that has almost been forgotten, but which, had it been followed up, would assuredly have led Ampère to anticipate by some years the great discovery of Faraday as to the induction of currents.

The experiment was first described by Ampère in October 1821, in a letter[†] to Van Beck. It had been tried in the preceding July. The following is Ampère's own first description of it:—

"Ce que cette expérience prouve directement, c'est que la proximité d'un courant électrique n'en excite point, par influence, dans un circuit métallique de cuivre, même dans les circonstances les plus favorables à cette influence. Voici l'expérience que je fis alors pour m'en assurer : je formai avec un long fil de cuivre A B C D E F [fig. 1], revêtu d'un ruban, une spirale B C D E dont les tours étaient séparés les

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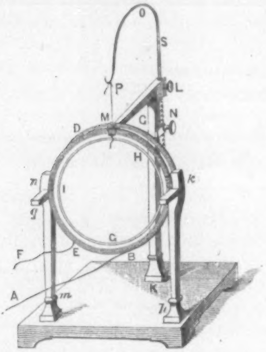
[*] Read April 26, 1895.

[†] *Journal de Physique*, t. xciii. p. 447, Oct. 1821. Reprinted at p. 212, vol. ii. of the 'Collection de Mémoires relatifs à la Physique, publiés par la Société française de Physique,' 1885.

uns des autres par la soie de ce ruban; je disposai cette spirale, comme on le voit dans la fig. 1, sur le pied en bois *h k m n*; les deux extrémités A et F de ce fil communiquaient avec celles de la pile de douze triades d'un pied carré, dont

Fig. 1.



je me suis servi pour la plupart de mes expériences. La partie supérieure de cette spirale était traversée par un petit tube de verre M, passant entre les spires qui se trouvaient les unes en avant et les autres en arrière de ce tube; un fil métallique très-fin le traversait sans en toucher les parois intérieures; il était attaché par un bout à la potence K S O P, qu'on faisait monter ou descendre à volonté en tournant le bouton N, et qu'on arrêtait à la hauteur convenable en serrant la vis de pression L; le cercle mobile G H I était suspendu au bout de ce fil, de manière à être concentrique à la spirale, situé dans le même plan, et très près des spires dont elle se composait. Le pied *h k m n* portait en outre deux petites règles *k p*, *n q*, sur lesquelles on pouvait appuyer les aimants qui devaient agir sur le cercle mobile. Cette disposition m'a paru la plus convenable pour exciter dans ce cercle des courants électriques par influence, si cela était possible; mais en le présentant à l'action d'un fort aimant,

je n'ai pas aperçu qu'il prit aucun mouvement, malgré la grande mobilité de ce genre de suspension."

The experiment of July 1821, being thus unsuccessful, was repeated in 1822 at Geneva, using a more powerful horseshoe magnet lent by Pictet. It is described by De La Rive* in the following terms:—

"La seconde expérience consiste dans l'influence qu'éprouve une lame de cuivre pliée en cercle de la part d'une ceinture de forts courans électriques au milieu desquels elle est suspendue, et qui l'entourent sans la toucher. Cette influence, que M. Ampère avait d'abord crue nulle, a été, à Genève, constatée par lui-même d'une manière très-précise. En présentant à un côté de cette lame un aimant en fer à cheval, très-fort, on l'a vue tantôt s'avancer entre les deux branches de l'aimant, tantôt au contraire en être repoussé, suivant le sens du courant dans les conducteurs environnans. Cette expérience importante montre donc que les corps qui ne sont pas susceptibles, au moyen de l'influence des courans électriques d'acquérir une aimentation permanente, comme le sont le fer et l'acier, peuvent du moins acquérir une sorte d'aimentation passagère pendant qu'ils sont sous cette influence †."

This note, which is textually repeated at p. 285 of Ampère's 'Recueil d'Observations,' is entirely vague on the crucial point whether the attractions and repulsions observed occurred only at times when the current was varying. By reprinting it textually (even the footnote about the instrument, which, however, he changed into the first person and signed with his initial "A"), Ampère accepted De la Rive's version and explanation of the Geneva experiment. Nevertheless a second version was given by Ampère himself* twelve days later on his return to Paris. This document lay unpublished in the Ampère manuscripts belonging to the Académie des Sciences until 1885. It reads as follows:—

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* Read to the 'Société de Physique et d'Histoire naturelle de Genève on Sept. 4, 1822; published first in the *Bibliothèque Universelle*, t. xxi. p. 29 (1822), then in the *Annales de Chimie et de Physique*, t. xxi. p. 47 (1822); reprinted by Ampère at p. 262 of his 'Recueil d'Observations électrodynamiques,' 1822, and again in the 'Collection de Mémoires,' t. ii. p. 328 (1885).

† "L'instrument dont M. Ampère s'est servi pour cette expérience est le même qu'il avait employé lorsqu'il l'essaya au mois de juillet 1820; il a été décrit et figuré dans le *Journal de Physique*." [This is a reference to *Journal de Physique*, xciii. p. 447, Dec. 1821, with a plate showing the apparatus. The same apparatus is depicted in fig. 17, plate vi., of Ampère's 'Recueil d'Observations électrodynamiques' (1822); and is described on p. 170 of that work. There is a discrepancy about the dates; July 1820 is here given, whereas Ampère's first date was given as July 1821.—S. P. T.]

"La troisième expérience avait pour objet de savoir si l'on peut produire un courant électrique par l'influence d'un autre courant. Il y a plus d'un an que je l'avais tentée, sans succès, avec l'appareil representé [fig. 1]; mais j'ai réussi avec un appareil absolument semblable, en employant l'excellent aimant en fer à cheval du musée de Genève, que m'avait procuré M. le professeur Pictet. Voici la description de cette expérience." [Here follows the description of the apparatus, word for word almost the same as that above in the description of the unsuccessful experiment of July 1821.] "Le circuit fermé placé sous l'influence du courant électrique dédoublé, mais sans aucune communication avec lui, a été attiré et repoussé alternativement par l'aimant, et cette expérience ne laisserait, par consequent, aucun doute sur la production des courants électriques par influence, si l'on ne pouvait soupçonner la présence d'un peu de fer dans le cuivre dont a été formé le circuit mobile. Il n'y avait cependant aucune action entre ce circuit et l'aimant avant que le courant électrique parcourût la spirale dont il était entouré; c'est pourquoi je regarde cette expérience comme suffisante pour prouver cette production; je me propose, néanmoins, pour prévenir toute objection, de la répéter incessament, avec un circuit formé d'un métal nonmagnétique très pur. Ce fait de la production de courants électriques par influence, très intéressant par lui-même, est d'ailleurs indépendant de la théorie générale de l'action électrodynamique."

There is a discrepancy between the first and second versions, in that while De la Rive says that the attractions and repulsions were in correspondence with the sense of the current in the coil (which we know could not be the case), Ampère says nothing about reversal of the current. As he attributed the effect to the possible presence of iron, it is clear he was expecting an effect due to the continued pressure of the current, not an instantaneous effect at make or break. We know now that this must have been so, and that an unvarying current could have produced no such effects as those described. That this should have escaped the notice not only of Ampère, but also of so skilled an experimenter as De la Rive, is remarkable. But the explanation of the phenomenon, as being due to a temporary magnetization acquired by the non-magnetic metal, given by De la Rive, and accepted by Ampère, is still more strange. Had no suggestion ever been made that there might possibly be an induction of currents by the action of a magnet, an explanation which ascribed the effects to a sort of temporary magnetism might have been more reasonable. But Ampère had himself already been looking for a possible inductive effect; nor was he alone in the idea that such might exist. Fresnel had on November 6th, 1820, announced to the Academy of Sciences that he had decomposed water by means of a magnet which was laid motionless within a spiral of wire. Emboldened by this announcement, Ampère remarked that he too had noticed something in the way of production of currents from a magnet. But before the end of the year these statements were withdrawn by their authors. Fresnel wrote* to the *Annales de Chimie* explaining the matter. He had surrounded a bar-magnet of steel with a spiral of iron wire, the ends of which dipped into water; and what he had announced on November 6th was that he had found one end of the iron wire to be discoloured and oxidized, while the other became covered with minute bubbles. He now finds that the announcement was premature, that the effects were not sustained by repeating the experiment, and, further, he says he does not believe in the success of Ritter's much earlier attempts to decompose water by a magnet. On behalf of M. Ampère, he added that the latter had indeed found little movements of a magnetic needle by bringing near it a circuit of copper wire (*laiton*) of which a portion was coiled in a spiral around a magnet, but that these movements were not repeated in any constant manner. Further, that these movements were, moreover, so feeble that Ampère would not have published the experiments if the success of Fresnel's, which he thought certain, had not persuaded him that these small agitations were occasioned also by an electric current resulting from the action of the magnet on the spiral in which it was enveloped.

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* Memoir presented to the Académie des Sciences, September 16, 1822; published for the first time in the 'Collection des Mémoires' by the 'Société française de Physique' (1885), t. ii. p. 329.

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* *Ann. Chim. Phys.* xv. 1820, pp. 219-222, "Note sur des Essais ayant pour but de décomposer l'eau avec un aimant."

This having occurred in 1820, it is clear that when making the Geneva experiment in 1822 Ampère must have had before him the possibility of induced currents, and chose rather the explanation of a temporary magnetism conferred on the copper loop.

Others in the meantime had tried to repeat Fresnel's observation, and found it erroneous.

Gilbert*, after giving an abstract of Fresnel's reputed discovery, says that he repeated the experiment without finding any discoloration of the iron wire, and concluded that the announcement was premature. Similar conclusions were arrived at by Pohl†.

A year or two later, when Arago's rotations were attracting the attention of experimenter, Becquerel ‡ investigated the supposed magnetism of bodies by taking small pieces of them, which he hung within a multiplier-coil of wire in place of the usual magnetic needle, and then turning on a current observed whether they moved or not. He found signs of magnetic action in needles made of peroxide of iron, copper, wood, and even shellac. After narrating his own experiments, he alluded to the Geneva experiment of Ampère, on p. 272, in the following terms:—

"Il résulterait de cette expérience, vu l'action semblable exercée par les deux poles de l'aimant en fer à cheval sur une même portion du circuit, que l'influence du courant électrique aurait développé dans la lame un autre courant électrique, tel qu'on en observe dans un fil métallique qui communique avec les deux poles d'une pile voltaique; mais

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* Gilb. *Ann.* xlvi. p. 410.

† Oken's *Isis*, 1822, pt. iv. p. 407. Also see remarks signed "P" at the end of an article by Savary in Pogg. *Ann.* viii. p. 368 (1826).

‡ *Ann. Chim. Phys.* xxv. p. 269.

M. Ampère s'est assuré depuis qu'il n'en est pas ainsi." What steps Ampère had in the meantime taken to assure himself that induction currents did not exist, Becquerel did not state, however.

In 1831 came Faraday's discoveries of the induction of currents by magnets, of the induction of currents by other currents, and of the cause of Arago's rotations. A group of notes* on these discoveries is to be found in December 1831 in the *Annales de Chimie.* It is curious to note the change of views. Becquerel and Ampère's communication to the Academy of January 23, 1832, appears along with abstracts of Faraday's work, and with an account of the experiments of Nobili and Antinori. There is an epitome of facts observed by Becquerel, and another of things to be looked for, by Ampère. This is followed by the following :—"Expériences sur les Courans électriques produits par l'influence d'un autre Courant," par M. Ampère. This article gives a third version of the Geneva experiments.

"Pendant mon séjour à Genève au mois de septembre 1822, M. Auguste de la Rive voulut bien m'aider dans des expériences que je désirais de faire sur la production d'un courant électrique par l'influence d'un autre courant. . . . Nous présentions à ce cercle un fort aimant en fer à cheval, de manière qu'un de ses poles se trouvait au dedans et l'autre au dehors du cercle. Dès que nous faisions communiquer avec la pile les deux extrémités du fil conducteur le cércle était attiré ou repoussé par l'aimant, suivant le pole qui répondait à l'intérieur du cercle : ce qui démontrait l'existence du courant électrique qui y était produit par l'influence du courant du fil conducteur. La découverte que vient de faire M. Faraday des courans électriques produits par l'influence d'un aimant, courans qu'avait obtenu Fresnel en 1820, mais qu'il n'avait pas cru suffisamment constatés par ses expériences, m'a porté naturellement à employer le galvanoscope multiplicateur, dont l'illustre chimiste anglais a fait usage, pour constater de nouveau et étudier dans toutes ses circonstances la production d'un courant électrique par un autre courant."

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* *Ann. Chim. Phys.* xlviii. 1831, pp. 405-428 ; see also Pogg. *Ann.* xxiv. 1832, p. 612, and particularly p. 614.

Ampère seems to have considered that the oxidation at first alleged by Fresnel was caused by induction currents arising from the diurnal variations of the magnetism of the stationary magnet. But it is evident that the electromotive forces due to any such cause would be of an order of magnitude utterly inadequate for the purpose. Further, as such currents must necessarily have been in alternate directions during the rise and fall of temperature, the total chemical action at the end would in no way depend upon the intermediate charges, but only upon the difference between the initial and final temperatures. Hence the total electromotive impulse tending to chemical action must have been infinitesimal compared with that due to simply removing the magnet once from the circuit! The third version differs from the former in describing the position of the magnet, and saying that the magnet (which in the original Ampère experiment was brought up after the current had been turned on) was placed in position *before* the circuit was completed.

From that time forward Ampère's experiment seems to have passed into oblivion. One reference to it, however, appeared in 1872, which gives a fourth version, differing not only from the three former, but accompanied by a picture and description of a very different form of apparatus. This description, from the pen of the usually accurate M. Verdet, is to be found at p. 357 of his well-known *Conférences de Physique*. It runs as follows:—

"209. *Expérience d'Ampère et De la Rive.*—Longtemps avant l'époque où Faraday fit la découverte de l'induction, Ampère et De la Rive * avaient fait une expérience relative à ces phénomènes et qu'ils n'avaient pas comprise. Ces physiciens cherchaient s'il y avait une action des courants sur des conducteurs placés à distance, par analogie avec les effets d'influence de l'électricité ordinaire; ils entreprirent une série d'expériences avec l'idée préconçue que le phénomène produit par le passage du courant dans un conducteur voisin serait permanent, c'est à dire persisterait pendant tout le temps que le courant traverserait le conducteur; ayant au contraire observé un phénomène instantané, ils regardèrent ce résultat comme un fait singulier ne méritant pas une étude ultérieure. Voici en qui consistait leur expérience : un fil fin de cuivre enroulé en anneau A [fig. 2] était suspendu à un fil de soie sans torsion OC, devant la base d'un électro-aimant BB′, de manière que les plans des spires de l'electro-aimant fussent parallèles au plan de l'anneau. A l'instant où le courant était lancé dans l'électro-aimant, l'anneau était repoussé ; mais cette déviation ne persistait pas, et bientôt le fil revenait rigoureusement à la verticale. Si l'on interrompait le courant, on observait une attraction aussi peu persistante que la répulsion."

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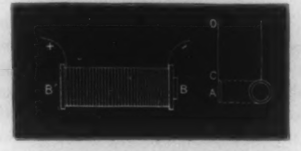
* *Bibliothèque Universelle*, septembre 1822, et *Annales de Chimie et de Physique* [2], t. xxi. p. 47 (1822), et t. xxv. p. 272 (1824).

Fig. 2.



The anachronism of representing a soft-iron electromagnet as having been used in 1822 is the strangest part of this description. But the experiment, as described by Verdet, is of interest as being a sort of forerunner of the actions observed in 1884 by Boys*, and in 1887 by Elihu Thomson.

I have repeated the experiment of Ampère in the form originally shown to De la Rive. It is quite easy of performance : but the relatively great moment of inertia of the copper circle masks the purely transitory effect of the impulse which the ring receives each time the current is turned on or off in the outer coil.

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* "A Magneto-electric Phenomenon." Proc. Phys. Soc. vol. vi. p. 218, 1884 ; Phil. Mag. [5] xviii. p. 216.

## XLIII. *A Theory of the Synchronous Motor.*

*By* W. G. RHODES, *M.Sc.*[*]

1. SEVERAL foreign writers, notably Steinmetz[†], have given theories of the synchronous motor, but most of them, by failing to see how the analysis could be simplified, add to the difficulties of the theory by mathematical intricacies which are apparently quite unnecessary. The author offers the following attempt to present a theory of the synchronous motor in as simple a way as possible, and as the mathematics for the most part consists of simple algebra, the difficulties are reduced to a physical conception of the subject. Many of the results have already been obtained, and the part for which the author chiefly claims originality is the method of attacking the problem.

2. We consider the case of an alternating-current machine whose field is excited by a direct current, while a simple alternating current passes round the armature.

Let $p =$ output of motor ;
$c =$ virtual value of armature current ;
$R =$ resistance of armature ;
$E =$ virtual value of impressed E.M.F. ;
$e =$ „ „ counter E.M.F. ;
$L =$ coefficient of self-induction of armature ;
$n =$ frequency of armature current ;
$I =$ impedance of armature $= \{R^2 + (2\pi nL)^2\}^{\frac{1}{2}}$ ;
$S =$ reactance $= 2\pi nL$ ;
$\psi =$ phase-difference between $c$ and $E$ ;
$\phi =$ „ „ $c$ and $e$ ;
$\theta =$ „ „ $c$ and $Ic$.

Then the input $= p + c^2R$ ;

and also $= cE \cos\psi$ ;

therefore $$p + c^2R = cE \cos\psi.$$

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[*] Read April 26, 1895.

[†] Trans. Am. Inst. Elec. Eng., December 1894.

Solving for $c$ we get

$$c = \frac{\mathrm{E}}{2\mathrm{R}}\cos\psi \pm \frac{1}{2\mathrm{R}}\sqrt{\{\mathrm{E}^2\cos^2\psi - 4p\mathrm{R}\}}. \quad . \quad . \quad (1)$$

Since $c$ is always real, we must have

$$\mathrm{E}^2\cos^2\psi \geqq 4p\mathrm{R};$$

therefore the maximum value of $p$ is

$$p = \frac{\mathrm{E}^2}{4\mathrm{R}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

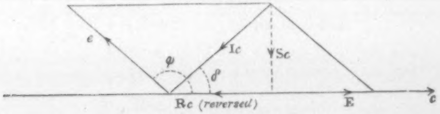
This occurs when $\psi = 0$; that is, when the current and the impressed E.M.F. are in phase with each other.

3. We notice that the maximum output is the same as the maximum energy which can be given to an external circuit by a generator of constant E.M.F., E. From (1) we get the corresponding value of the current

$$c = \frac{\mathrm{E}}{2\mathrm{R}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

To find the corresponding value of $e$ we notice that E, $e$, and I$c$ (the resultant of S$c$ and R$c$ reversed) are in equilibrium

Fig. 1.



amongst themselves; so that taking components of these along and at right angles to the direction of E, we have

$$\left.\begin{aligned} -e\cos\phi &= \mathrm{E} - \mathrm{R}c \\ \text{and} \qquad e\sin\phi &= \mathrm{S}c \end{aligned}\right\};$$

$$\left.\begin{aligned} \text{therefore} \qquad e\cos\phi &= 2\mathrm{R}c - \mathrm{R}c = \mathrm{R}c \\ \text{and} \qquad e\sin\phi &= \mathrm{S}c \end{aligned}\right\}\text{from (3).}$$

Squaring and adding, we get

$$e^2=(R^2+S^2)c^2=I^2c^2,$$

therefore

$$e=Ic=\frac{IE}{2R}. \qquad \qquad (4)$$

Also, by division,

$$-\tan\phi=\frac{S}{R}=\tan\theta \text{ (see fig. 1)}.$$

4. We thus find that when working at maximum output:—

(1) The impressed E.M.F. is in phase with the current in the armature.

(2) The maximum output is $p=\frac{E^2}{4R}$.

(3) The corresponding current in armature is $c=\frac{E}{2R}$.

(4) The corresponding counter E.M.F. is $e=\frac{IE}{2R}$.

(5) The angle of phase between the armature-current and the E.M.F. necessary to overcome the resistance and self-induction of the armature is equal and opposite to the angle between the current and the counter E.M.F.

(6) Also from (4) we see that

$$e \gtreqless E \text{ according as } I \gtreqless 2R,$$

that is according as $(2\pi nL)^2+R^2 \gtreqless 4R^2$,

" " $L^2 \gtreqless \frac{3R^2}{4\pi^2n^2}$,

" " $L \gtreqless \frac{R\sqrt{3}}{2\pi n}$.

*Running Light.*

5. We have

$$\left.\begin{array}{r} p+c^2R=cE\cos\psi \\ p=ce\cos\phi \end{array}\right\}.$$

and

If we neglect the friction of the bearings &c., we may, in this case, put $p=0$; we then have

$$\phi=\pm\frac{\pi}{2}$$

and

$$cR = E \cos \psi.$$

Hence the maximum value of $c$ is (putting $\psi = 0$)

$$c = \frac{E}{R},$$

the same as would be produced by a constant E.M.F. E in a non-inductive circuit of resistance R.

Also putting $\psi = \pm \frac{\pi}{2}$, the minimum current is zero.

Now, from fig. 1, we get (of course E and $c$ are not now in phase)

$$E^2 = e^2 + I^2c^2 + 2Ice \cos(\theta - \phi);$$

when $\phi = \pm \frac{\pi}{2}$, this becomes

$$\begin{aligned} E^2 &= e^2 + I^2c^2 \pm 2Ice \sin \theta \\ &= e^2 + I^2c^2 \pm 2Sce, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5) \end{aligned}$$

since $\sin \theta = \frac{S}{I}$.

The upper sign in (5) corresponds to the machine running as a generator, and the lower sign as a motor.

We also see from (5) that corresponding to $c = \frac{E}{R}$ we have

$$e = \mp \frac{ES}{R},$$

and, corresponding to $c = 0$, we have

$$e = \pm E.$$

Now, solving equation (5) as a quadratic in $c$ we get

$$c = \mp \frac{eS}{I^2} \pm \frac{1}{I^2} \sqrt{(I^2E^2 - R^2e^2)}, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and, as $c$ is real, we must have

$$I^2E^2 \geqq R^2e^2$$

or

$$IE \geqq Re;$$

therefore the maximum value of $e$ is given by

$$e = \pm \frac{IE}{R}$$

and the corresponding current is

$$c = \mp \frac{eS}{I^2}$$

$$= \mp \frac{SE}{RI}.$$

The equation

$$e^2 - 2Sce + I^2c^2 = E^2$$

is the characteristic curve of the motor running light. It may be written

$$e^2 - 2Sce + S^2c^2 + R^2c^2 = E^2$$

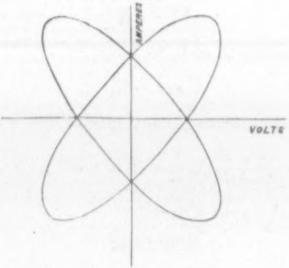
or $$(e - Sc)^2 + R^2c^2 = E^2,$$

or $$\frac{(e-Sc)^2}{E^2} + \frac{c^2}{\frac{E^2}{R^2}} = 1,$$

which is the equation to an ellipse having as conjugate diameters the lines

$$e - Sc = 0 \text{ and } c = 0.$$

Fig. 2.



Similarly, the equation

$$e^2 + 2Sce + I^2c^2 = E^2,$$

which refers to the generator, may be written

$$\frac{(e+Sc)^2}{E^2}+\frac{c^2}{\frac{E^2}{R^2}}=1,$$

also the equation to an ellipse. These ellipses are represented in fig. 2.

*Minimum Current at Given Power.*

6. We have

$$p+c^2R=Ec\cos\psi.$$

The current is a minimum when $\frac{dc}{d\psi}=0$. Now, differentiating with respect to $\psi$,

$$(2cR-E\cos\psi)\frac{dc}{d\psi}+Ec\sin\psi=0;$$

therefore, when $\frac{dc}{d\psi}=0$, we have

$$\sin\psi=0,$$

or

$$\psi=0;$$

that is, the current is a minimum when in phase with the impressed E.M.F., as is otherwise obvious. Putting, therefore, $\psi=0$, we have

$$p+c^2R=Ec. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This curve is of the second degree in $c$ and $p$, and is satisfied by the following system of points:—

$$(a)\ \left.\begin{matrix}c=0,\\p=0,\end{matrix}\right\}\qquad(b)\ \left.\begin{matrix}c=\frac{E}{2R},\\p=\frac{E^2}{4R}\end{matrix}\right\}\qquad(c)\ \left.\begin{matrix}c=\frac{E}{R},\\p=0.\end{matrix}\right\}$$

That the equation is satisfied by ($a$) is obvious, and we see that it is satisfied by the points ($b$) and ($c$) by writing it in the form

$$\left(c-\frac{E}{2R}\right)^2+\frac{p}{R}=\frac{E^2}{4R^2}.$$

7. Thus we see that the curve of minimum current at given power passes through the points of

($a$) zero current and zero power;
($b$) maximum power;
($c$) maximum current and zero power.

We notice that the maximum current at no load is $c=\frac{\mathrm{E}}{\mathrm{R}}$, whereas if the motor were at rest the current would be $c=\frac{\mathrm{E}}{\mathrm{I}}$; that is, the maximum current at no load is in all cases greater than the maximum current if the armature is at rest.

8. Again, from the equation

$$p+c^2r=c\mathrm{E}\cos\psi$$

we have

$$\psi=\cos^{-1}\frac{p+c^2r}{c\mathrm{E}},$$

therefore

$$\frac{d\psi}{dc}=\frac{c^2r-p}{c\sqrt{\{c^2\mathrm{E}^2-(p+c^2r)^2\}}}$$

$$=0$$

when

$$p=c^2r.$$

$\psi$ is then a maximum, and we see that the maximum difference of phase between the current and the impressed E.M.F. takes place when the electrical efficiency is $\frac{1}{2}$.

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9. *Example.*—Suppose we have a 50 kilowatt motor driven by a 1000 volt generator, and suppose that $\mathrm{R}=3$ ohms and $\mathrm{S}=4$ ohms, so that $\mathrm{I}=5$ ohms.

Then maximum output . . $=\frac{10^6}{12}=$ 83·3 kilowatts.

Corresponding current . . $=\frac{1000}{6}=$ 166·7 amperes.

" counter E.M.F. $=\frac{5000}{6}=$ 833·3 volts.

Maximum current running light $=\frac{1000}{3}=$ 333·3 amperes.

Corresponding counter E.M.F. $=\frac{4000}{3}=$ 1333·3 volts.

&c.

10. To find the characteristic of the motor at any given load we must eliminate $\theta$ and $\phi$ between the equations

$$\left.\begin{aligned} p&=ce\cos\phi,\\ \sin\theta&=\frac{S}{I},\\ \text{and}\qquad E^2&=e^2+I^2c^2+2Ice\cos(\theta-\phi). \end{aligned}\right\}$$

The eliminant is

$$E^2-e^2-I^2c^2-2Rp=2S\sqrt{c^2e^2-p^2}, \quad . \quad . \quad . \quad (8)$$

which is the required general relation between $e$ and $c$.

11. In the paper referred to above, Steinmetz calls equation (8) the Fundamental Equation of the Synchronous Motor: the equation is there developed and plotted; results are obtained directly from equation (8), but the development is so cumbrous that the writer thinks that his simple treatment may benefit those interested in the subject of Alternate Current Motors.

## DISCUSSION.

Prof. S. P. THOMPSON said that the mathematical part of the paper was much simpler than that in previous investigations on this subject, and the method of arriving at the results by rejecting imaginary roots of the equations was particularly neat and instructive. The part of the paper relating to armature reactions and phase relationships was quite new. Two results deserved special attention; first, that the maximum current of zero power was the same as if the circuit was non-inductive; second, that the maximum current at zero power was double the current corresponding to maximum output.

Mr. BLAKESLEY said that the paper did not consider the stability of the system, and he thought some of the results corresponded to regions of instability.

## XLIV. *A Theory of the Synchronous Motor.* *By* W. G. Rhodes, *M.Sc.*[*]

[Continued from p. 509.]

### *Armature Reaction in a Single Phase Alternate Current Machine.*

12. In the foregoing analytical treatment the magnitudes only of $\theta$, $\phi$, and $\psi$ are considered. We proceed to investigate the signs of these angles in order to determine the lags or leads of the E.M.F.'s over the current and to apply the results to find out whether the field excitation of generator and motor is strengthened or weakened by the reaction of the armature currents.

13. It will now be convenient to slightly alter the meanings of the symbols.

Let E = virtual value of generator E.M.F.
$e$ = „ „ counter E.M.F. of motor (as before);
R = total resistance in circuit consisting of generator, motor, and line:
L = sum of coefficients of self-induction of generator and motor armatures; or, if the line possesses self-induction, the coefficient of self-induction of the whole circuit;
I = impedance of the complete circuit;
S = reactance of the complete circuit.

14. The E.M.F. R$c$ which drives the current is the resultant of E, $e$, and S$c$; so that E, $e$, S$c$, and R$c$ reversed form a system of E.M.F.'s in equilibrium.

In fig. 3 let the positive direction of rotation be counter-clockwise, and let O$c$ be the direction of the current. The instantaneous value of the current does not concern us at present. Take OR′ equal to R$c$ reversed, and consequently opposing the current; let OS′ = S$c$, lagging behind the current by a quarter of a period. The resultant, OT′, of OR′ and OS′ will then be equal and opposite to the resultant of E and $e$. If, therefore, we produce T′O to T and make OT = OT′, OT will represent in magnitude and direction the resultant of E and *e*. If, now, we are given the magnitudes of E and *e* we can find their directions by the parallelogram law. Now two parallelograms can be constructed having OT as diagonal and E, *e* as adjacent sides, but, since E is the E.M.F. of the generator, we take that which gives the component of E along Oc in the same sense as the current. The other parallelogram would make *e* the generator. We may notice that the possibility of constructing these two parallelograms affords a proof of the fact that, in general, either of two alternate current machines may be driven as a motor by the other, irrespective of their relative E.M.F.'s. An analytical proof of this is given by the energy equation

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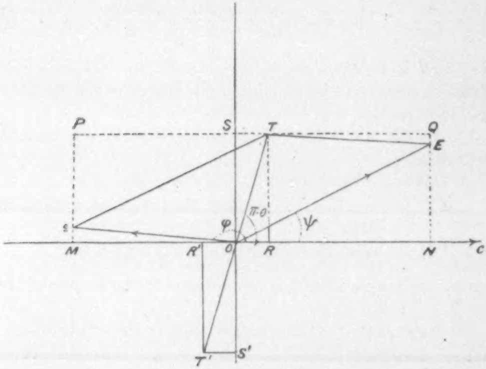
[*] Read June 28, 1895.

Fig. 3.



$$p + c^2 R = cE\cos\psi,$$

remembering that

$$p = ce\cos\phi,$$

and that $\phi$ and $\psi$ are independent.

The condition that E represents the generator E.M.F. limits our choice of the two parallelograms to OET*e* (fig. 3).

We then have

$$\text{angle } c\mathrm{OE} = \psi,$$

$$\text{angle } c\mathrm{OT}' = \theta,$$

and

$$\text{angle } c\mathrm{O}e = \phi.$$

15. Now through T draw PSTQ parallel to the line of current, and draw PM, SO, TR, and QN through $e$, O, T, and Q respectively, at right angles to the line of current.

We have

$$\tan\theta = -\frac{\mathrm{S}c}{\mathrm{R}c} = -\frac{\mathrm{S}}{\mathrm{R}} = -\frac{2\pi n\mathrm{L}}{\mathrm{R}}, \quad . \quad . \quad . \quad (9)$$

that is, $\theta$ is independent of the current and OT is a fixed direction relative to O$c$ so long as the speeds of the machines are kept constant, and L is considered constant.

16. In fig. 3, OS (or PM) is proportional to the current, $[=2\pi n\mathrm{L}c]$;

OM is the component of $e$ directly opposing $c$,
OR is the E.M.F. required to overcome resistance, $[=\mathrm{R}c]$;
and ON is the component of E in the direction of $c$;

hence, rectangle PSOM is proportional to the output of the motor $[p]$;
rectangle OSTR is proportional to the $c^2$R losses;
and rectangle OSQN " " output of generator $[c\mathrm{E}\cos\psi]$.

From this, and the equation

$$p + c^2\mathrm{R} = c\mathrm{E}\cos\psi,$$

it follows that the efficiency of transformation

$$= \frac{\mathrm{OM}}{\mathrm{ON}} = \frac{\mathrm{OM}}{\mathrm{MR}}.$$

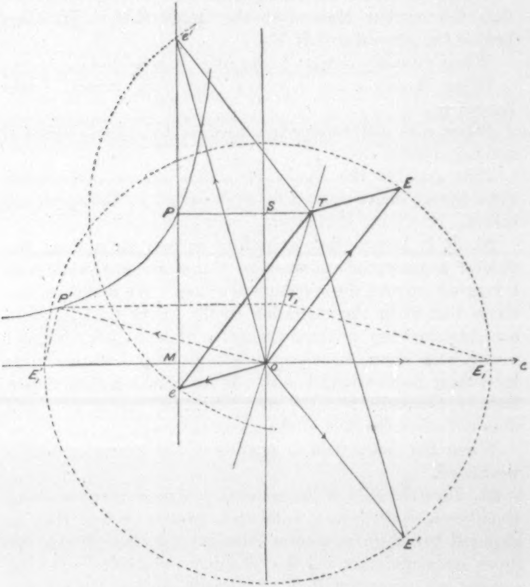
17. If the output of the motor is kept constant, we have

$$\text{rectangle PSOM} = \text{constant},$$

and the locus of P is a rectangular hyperbola having OM and OS as asymptotes (fig. 4).

Take any point P on this hyperbola. We have seen (9) that OT has a fixed direction relative to O$c$; and the point T (fig. 3) on this direction is found by drawing through P a line parallel to O*c*. Again, *e* lies on the line through P parallel to OS and *e*T = E, in magnitude. Let the E.M.F. of the generator be kept constant and equal to E. With centre T and radius E describe a circle cutting PM in *e* and *e′*; then the corresponding counter E.M.F. of the motor may be

Fig. 4.



either O*e* or O*e′*, and the current is represented in magnitude by PM: that is corresponding to given values of E and *c* there are two values of *e*. The relative phases in the two cases are shown in the parallelograms O*e*TE and O*e′*TE′ (fig. 4).

18. To find the point P′ on the hyperbola corresponding to

minimum current we have to bring the points $e$ and $e'$ into coincidence. The point $P'$ is obviously got by taking $OE_1'$ equal to E and through $E_1'$ drawing $E_1'P$ parallel to OT. The resulting parallelogram $OP'T_1E_1$ shows that the generator E.M.F. is in phase with the current.

19. Suppose now that the excitation of the generator field is kept constant while that of the motor is varied.

When the motor excitation is small, as $Oe$ (fig. 4), we see that the current leads over the motor E.M.F. and lags behind the generator E.M.F.

When $e$ exactly opposes $c$, the latter lags behind E.

When E and $c$ are in phase (minimum current), $c$ lags behind $e$.

When $e$ is still further increased, as $Oe'$, $c$ leads before E and lags behind $e$.

This explains the condenser action of an over-excited synchronous motor noticed by Professor S. P. Thompson and others.

20. It is known that a leading current strengthens the field of a generator and weakens that of a motor, while with a lagging current the reverse is the case. We therefore conclude that when the excitation of the motor field is small, armature reaction weakens the fields of both generator and motor, and when the motor is over-excited both machines have their fields strengthened. When working at minimum current, armature reaction strengthens the motor field and does not affect the field of the generator.

When the motor field is unaffected, the generator field is weakened.

21. Now the field of the motor is, under ordinary working conditions, excited to a somewhat greater extent than is required to obtain minimum current; for, though the $c^2R$ losses are a minimum and the efficiency a maximum when the current is a minimum, it is advisable to increase the counter E.M.F. to a certain extent in order to cope with accidental variations of the load. Under ordinary working conditions, therefore, the effect of armature reaction is to strengthen the field of the motor and also of the generator, but to a less extent.

22. We now proceed to obtain an expression for the altera-

tion, in ampere turns, of the field excitation due to armature reaction.

Let $\phi$ be the displacement of phase of the current over the E.M.F. of the machine; $n$ the number of turns of wire in one section of the armature; $i$ the virtual current, and $i_0 \sin pt$ the instantaneous value of the current, so that $i_0$ is its maximum value.

It has hitherto been customary to assume that the alteration in the excitation is given by the expression

$$in\phi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where $\phi$ is expressed in circular measure.

Now it is not the *virtual* current to which the armature reaction is due, but the *mean value of the current* through an angle $\phi$ on each side of its maximum value; that is, the proper value of the current is given by

$$\mathrm{I} = \frac{p}{2\phi}\int_{\left(\frac{\pi}{2}-\phi\right)\frac{1}{p}}^{\left(\frac{\pi}{2}+\phi\right)\frac{1}{p}} i_0 \sin pt\, dt$$

$$= \frac{i_0}{\phi}\sin\phi.$$

And, remembering that $i_0 = \sqrt{2}\,.\,i$, we get

$$\mathrm{I} = \frac{\sqrt{2}\,.\,i}{\phi}\sin\phi.$$

Thus the proper expression for the alteration of the field excitation in ampere turns is

$$2\mathrm{I}n\phi$$

or

$$2\sqrt{2}\,in\sin\phi. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

To find the total excitation of the field we must add expression (11) to or subtract it from the ampere turns on the field according as the current leads or lags in a generator, and lags or leads in a motor.

## DISCUSSION.

Mr. TUNZELMANN expressed a hope that the author would amplify parts of his paper.

Mr. BLAKESLEY said the conclusion of the author, that "either of two alternate current machines may be driven as a motor by the other, irrespective of their relative E.M.F.'s," is not invariably correct. The facts of the case were these:—The E.M.F. of the motor may exceed that of the other machine to a certain extent; but that E.M.F. multiplied by the cosine of the angle of electric lag must yield a product not greater than the E.M.F. of the generator,—*i. e.*, using Mr. Rhodes's symbols, $e \cos \theta$ must not be greater than E. Mr. Blakesley gave a geometrical proof of this; but the same proposition had been given by him some ten years ago, in the course of investigating the subject generally. This was at a time when Dr. John Hopkinson was, with less than his usual perspicuity, teaching that synchronous alternate current machines could not be run in series with stability, both doing work. Referring to the author's diagrams, Mr. Blakesley said that in a problem involving so many elements as that under consideration, it was impossible, with the limited dimensions of space, to represent the results with the complete generality of a formula. Some elements had to be taken as the independent, others as the dependent, variables. The author had considered the power transmitted to the motor, the E.M.F. of the generator, and the angle of electric lag, as independent; the E.M.F. of the motor as dependent. In Mr. Blakesley's original diagrams the E.M.F.'s were both considered independent, as well as the electric lag, and the powers applied or transmitted as dependent variables. In any case the formulæ properly derived from such diagrams became perfectly general, and it did not appear to him that the change of method indicated could properly be called a new theory on the subject. As a matter of fact, diagrams based on the independence of the E.M.F.'s and the electric lag would furnish a better means of discussing the question of the stability of the motion than Mr. Rhodes's plan, and this might account for the entire omission from the paper of this important matter.

Prof. S. P. Thompson said it was impossible to discuss the question of stability till the subject of armature reaction had been thoroughly investigated. The terms lag and lead had been used by Mr. Rhodes in a consistent manner; but this was not always done, and he recommended that the phase of the current which was common to both generator and motor be taken as the standard.

The Author, in his reply, said he agreed with Mr. Blakesley that there was a limit to the extent to which the motor might be excited, and this upper limit could easily be obtained from the figure given in the paper. The question of armature reaction was, however, most important, as it might excite the field two or three times more than the original excitation. Since motors were designed to do a certain amount of work, and not the work to fit the motor, it was most natural to take the output of the motor as fixed.

## XLV. *On the Use of an Iodine Voltameter for the Measurement of Small Currents.*

*By* E. F. Herroun, *F.I.C., Professor of Natural Philosophy, Queen's College, London*[*].

The instruments in general use for the direct measurement of currents by electrolysis, as in the determination of reduction factors of galvanometers, comprise the hydrogen, silver, and copper voltameters: each of these possesses certain advantages, but none is free from defect. When occasion arises to make a large number of determinations of relatively small currents, the difficulties attending their use become more manifest.

Some of the defects of the ordinary types may be briefly stated. The hydrogen voltameter, consisting of platinum plates immersed in dilute sulphuric acid, has the following disadvantages:—

1. It acquires a large counter electromotive force of polarization, so that the current, on first joining up, is very inconstant.

2. Its internal resistance is subject to considerable fluctuations, according to the rate and mode of disengagement of the electrolytic gases.

3. Oxygen present in the dilute acid, or migrating from

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[*] Read May 10, 1895.

the anode, diminishes the amount of hydrogen collected, and so causes the current to be underestimated.

4. When small currents are being measured, the bubbles which cling to the electrodes or sides of the graduated tube cause an appreciable error.

5. Calculation of the current-strength is rendered difficult owing to the necessity for correcting the volume of gas for temperature, barometric pressure, and for the tension of vapour of the dilute acid employed, which last is frequently not exactly known.

In the silver voltameter the foregoing objections do not hold, with the exception of No. 3; for dissolved oxygen has been found to affect the yield of silver, a greater amount being obtained when the electrolysis is conducted *in vacuo* or hydrogen than in air. But in the silver voltameter the experimental difficulties in washing, drying, and weighing, it may be only a few centigrammes of silver, involve a large expenditure of time; or if the weight of deposited silver be increased by prolonging the current, the difficulty of maintaining it constant is greater.

The difficulties which exist with silver are still more apparent with copper; for, as its chemical equivalent is much smaller, the weight of copper yielded by a given number of coulombs is only $\frac{31 \cdot 75}{108}$ of the weight of silver. In addition, its greater readiness to oxidize may cause the deposit of copper to become superficially oxidized in the process of washing and drying. This, however, may partly compensate for the defect in weight due to dissolved oxygen round the kathode.

If a list of the electrochemical equivalents of elements be examined, next to mercur*ous* mercury, the one which has the highest value will be found to be iodine; and it is curious that, although the liberation of iodine from potassic iodide was very early used to detect electric currents, no attempt in recent years seems to have been made to utilize it for quantitative measurements.

As iodine is an anion, dissolved oxygen, which diminishes the yield at the kathode in other voltameters, will have no such action in a neutral solution of iodide; and as its colour reaction with starch is extremely sharp, and its titration with standard sodium thiosulphate a process of greater accuracy than the performance of the average balance, the exact determination of the amount of iodine liberated by a current is both easy and rapid.

## EXPERIMENTAL DETAILS.

A voltameter consisting of platinum plates in a solution of potassic iodide is not suited for quantitative measurement; as, upon electrolysis, it yields caustic potash and hydrogen at the kathode, the former of which by diffusion would come in contact with the iodine set free at the anode, converting it into iodide and iodate. If this were all it would be easy to acidify after electrolysis, when the iodine would be again set free; but there is besides the additional disadvantage, that a rather large electromotive force of polarization is set up between the electrode surrounded by hydrogen and KOH and the one surrounded by iodine.

The solution actually employed was a 10 per cent. to 15 per cent. solution of neutral zinc iodide (a solution that keeps well if a small strip of zinc be suspended in it). The anode was a plate or disk of platinum placed at the bottom of a tall narrow beaker and joined by a platinum wire, sealed through a glass tube extending beyond the top of the beaker, to the outside circuit. In this way all the iodine is liberated at the bottom of the column of liquid, and, owing to its high density, tends very little to diffuse upward. The kathode was a rod of amalgamated zinc, loosely jacketed with filter-paper or linen. The zinc rod should be supported so that it only dips a few centimetres into the top of the liquid, thus diminishing the liability of any of the liberated iodine coming in contact with it. The jacketing was found necessary to prevent particles of electro-deposited zinc becoming detached and falling into the solution of iodine at the bottom of the cell.

When used with currents not exceeding $\frac{1}{20}$ of an ampere and an anode of 9 square centimetres, it was found that no iodine diffused up to the level of the kathode in experiments of over an hour's duration, the cell being kept completely at rest. With feebler currents, lasting for a protracted time, it was found advisable to use a U-tube with a good plug of asbestos in the bend, filled with the zinc-iodide solution and having a platinum plate and zinc rod in the two sides of the tube ; but naturally with this form the resistance was much greater than with the beaker form.

With large currents "electric convection" leads to diffusion of the iodine through the whole liquid, and therefore the author does not consider it well adapted for their measurement, except for approximate, rapid determinations.

In the Report to the Board of Trade of the Electrical Standards Committee, the importance is pointed out, in using a silver voltameter, of having a considerable *wire*-resistance in the circuit to mitigate the effect of change of resistance in the voltameter itself: the same precautions apply to the iodine voltameter and a slight readjustment of the resistance at first employed is usually necessary to keep the current, as indicated by a galvanometer, constant. This is owing to a small change in the adverse electromotive force, but if a battery of fairly high E.M.F. (*ex. gr.* 3 Grove cells) be employed, controlled by a moderately large resistance, the current may be kept very constant.

After the iodine voltameter has been in circuit for a time which will vary with the degree of accuracy required and the actual strength of the current, the latter is stopped and the zinc kathode is immediately removed from the liquid. The solution is then stirred up, and the amount of free iodine determined by direct titration with standard sodium thiosulphate solution, after the addition of starch. Taking the electrochemical equivalent of iodine as ·001314 grm. per coulomb, a convenient strength of sodium thiosulphate solution is one of which each cubic centimetre reduces five times this amount (1 cub. centim. = ·00657 grm. I) : this corresponds to a solution containing 12·845 grms. of pure sodium thiosulphate per litre; but it is necessary to standardize it from time to time with a standard solution of iodine, as its value is liable to change somewhat on keeping.

As pure zinc iodide is not always readily obtainable, though it can be easily prepared, the author has found that a solution of 15 per cent. zinc chloride, to which about 5 per cent. potassic iodide has been added, may be substituted for pure zinc iodide. Any chlorine, even if liberated, which is improbable with small current-densities, would at once yield its equivalent in iodine without escaping, and should any caustic potash form at the kathode it would merely produce zinc hydrate and potassic chloride.

A single example of the accuracy and rapidity of the method, selected from laboratory notes, may here be given:—

"Dec. 19, 1894.—Current through calibrated galvanometer =20°.

Time current was passing = 2 hours.
Weight of silver deposited = 0·2122 grm.
Current (from above deposit) = 0·0264 ampere.

The same deflexion (20°) obtained using iodine voltameter.
Time = 30 minutes.

Iodine liberated required 9·6 cub. centim. of standard thiosulphate sol. $9{\cdot}6 \times 5 = 48$ coulombs. $\text{Current} = \frac{48}{1800^s} = 0{\cdot}026\dot{6}$ amp."

The latter result is seen to be in fairly close agreement with that obtained with the silver voltameter, but slightly higher, as was to be expected from the reasons stated above. It will be noticed that the duration of the experiment was only a quarter of that with the silver voltameter.

In conclusion the points which recommend the iodine voltameter in the author's opinion are as follows:—

1. Its freedom from the effect of dissolved oxygen which gives "low" results with kationic voltameters.

2. The relatively short duration of the current necessary to obtain results of fair accuracy.

3. The rapidity of the volumetric estimation of the liberated iodine.

4. The ease and rapidity in calculating the results.

## DISCUSSION.

Prof. CAREY FOSTER considered this process for measuring currents a most valuable one. The idea of using a volumetric method for measuring currents was, to him, new. He did not, however, see the advantage of using a substance with a high electro-chemical equivalent if a volumetric method was employed to estimate the quantity of the substance liberated. It would be possible to use a chloride, though in this case the titration would probably be less accurate.

Prof. SILVANUS THOMPSON said he thought the method would be very valuable, but he would like to know if any error was likely to arise if too great a current density was employed. The number the author had assumed for the atomic weight of silver (108) was only approximate; if the more accurate value 107·7 were used the agreement between the results obtained with the silver and iodine voltameters would be improved.

Mr. TROTTER asked what was the largest current that could be accurately measured.

Mr. ENRIGHT said he had used porous diaphragms in iodine voltameters, and found that the iodine collected in the positive compartment, while the water was driven over into the negative compartment. With strong currents it was possible to get almost pure iodine left in the one compartment.

Mr. WATSON thought that since the value for the electro-chemical equivalent of iodine used by the author was deduced from Rayleigh's value of the electro-chemical equivalent of silver, and that Rayleigh's experiments were performed in air, the difference obtained with the silver and iodine voltameters could hardly be due to the cause suggested.

Mr. ELDER warned the members that volumetric measurements were not so accurate or easy as they seemed. He particularly mistrusted a solution of sodium thiosulphate, since he had found a solution of this substance to change even in twenty-four hours. The difficulty of accurately reading the burette might be overcome by weighing the burette and its contents before and after the titration.

The Author, in his reply, said that with the size of electrodes he used (about 9 sq. cm. surface), 0·1 ampère was the maximum current it was safe to use. The only substance likely to be produced by too great a current density was periodate, which, since it was insoluble, would immediately be noticed. The influence of the dissolved oxygen was only appreciable with small currents where the electrolysis lasts some time ; while in Rayleigh's experiments large currents were employed.

The CHAIRMAN, while returning thanks to the author for the paper, mentioned that in his experience he had found zinc salts to be very untrustworthy.

## XLVI. *On the Condensation and the Critical Phenomena of Mixtures of Ethane and Nitrous Oxide.* *By* Dr. KUENEN[*].

1. BEFORE relating the results arrived at in this investigation I shall have to give a short account of the course of thought which led to the choice of the subject.

My experiments on the conduct of mixtures[†] are based upon the theory of Prof. van der Waals[‡]. Van der Waals "describes" the properties of mixtures by means of an isothermal surface, the coordinates of which are the composition of the mixture $x$ $(0<x<1)$, the volume $v$, and the free energy $\psi$ $(\psi=\epsilon-t\eta;\ \epsilon=$ energy, $\eta=$ entropy, $t=$ temperature). On this surface there appear *plaits*[§], which determine the coexistence of two or more phases. Those points of these plaits which have a common tangent plane represent the phases which may coexist at the temperature for which the surface is constructed, and at a pressure indicated by the slope of the tangent plane $\left(p=-\dfrac{\partial\psi}{\partial v}\right)$. The double curves traced out by rolling the tangent planes over the plaits are the so-called *connodal* curves. It may happen that the plaits terminate on the surface itself (*i. e.* between the planes for which $x=0$ and $x=1$). In that case the coexisting phases approach each other and at last coincide in a so-called *plaitpoint.* In studying the plaits on the surface, one may use the projection upon the $x$–$v$ plane. This projection consists of the $x$-axis between $x=0$ and $x=1$, the two $v$-axes for $x=0$ and $x=1$, the connodal curves with or without the plaitpoints. The points of the connodal curves belonging together may be joined by straight lines. The ratio of the parts into which these lines are divided by a line perpendicular to the $x$-axis, say for $x=x_1$, represents the ratio of the quantities of the two phases which will be formed when the mixture $x_1$ is taken at the pressure at which the two phases may coexist. Keeping this in view, it is easy to derive the condensation and critical phenomena of a mixture.

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[*] Read May 24, 1895.

[†] Kuenen, *Archives Néerl.* xxvi. pp. 354–422 ; *Zeitschr. phys. Chemie*, xi. pp. 38–48 ; *Verhand. Kon. Akad. Amsterdam*, passim ; Communications from the Labor. of Physics, Leiden, Nos. 4, 7, 13.

[‡] Van der Waals, *Archives Néerl.* xxiv. pp. 1–56 ; *Zeitschr. phys. Chemie*, v. pp. 133–173.

[§] For the nomenclature used in this treatise, *cf.* Korteweg, *Wien. Ber.* xcviii. pp. 1154–1191 ; *Archives Néerl.* xxiv. pp. 57–98.

2. We shall only discuss the very simple case here, that there is only one plait on the surface, the vapour-liquid plait, which determines the coexistence of a vapour-phase and a liquid-phase. The plait, roughly speaking, has the direction of the $x$-axis; its plaitpoint, which will make its appearance if only we raise the temperature to a sufficient height, need not coincide with the end of the plait, *i. e.* with that point of the connodal curve which is nearest to one of the $\psi v$ planes (in the projection = $v$-axis). The latter point was called *critical point of contact**. Now in deriving the critical phenomena two cases have to be distinguished depending on the relative position of these two points, which we shall call P and R. Either P is situated nearer to the $\psi x$ plane ($x$-axis) or this is the case with R.

3. In the first case the condensation of a mixture has the following character. Below a definite temperature (plaitpoint-temperature = $T_P$), different for every mixture, the quantity of the denser phase increases regularly during compression; the pressure rises, and both the composition and the volume of both phases change continuously. Above another temperature (temperature of the critical point of contact = critical temperature = $T^R$) there is no condensation possible. At temperatures ranging between $T_P$ and $T_R$ the condensation will have the following character:—With compression the

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* Kuenen, *Archives Néerl.* xxvi. p. 379; Communications from the Lab. of Physics, Leiden, No. 4, pp. 7 *sqq.*; *Zeitschrift phys. Chemie*, xi. p. 44.

quantity of the appearing liquid first increases, reaches a maximum value, and after that decreases till it disappears. This was called *retrograde condensation of the first kind* (r.c. I.)*. The nearer we get to the plaitpoint-temperature the larger becomes the quantity of the liquid and the smaller the difference between the phases, apparent from a less distinct liquid surface between the phases. A mixture, therefore, has a critical region instead of one critical point, lying between two critical temperatures.

4. The phenomena predicted in this manner were then observed by me in mixtures of carbonic acid and methyl chloride†, and afterwards of carbonic acid and air‡. The deviation from what had been observed by former experimenters, viz., the flattening and disappearing of the liquid surface throughout the critical region without retrograde condensation, was explained by retardation§, which was annihilated in my experiments for the first time by means of a small iron stirring-rod within the tubes, which was moved by an electromagnet outside the tubes.

5. If P lies on the other side of R there are again two definite critical temperatures, $T^P$ and $T_R$, for every mixture; but the process of condensation between those two will be different from what it was in the first case. By compression a new phase appears of a larger volume‖ this time, *i. e.* a vapour-phase, which begins by increasing, then reaches a maximum, and then again diminishes and disappears. This was called *retrograde condensation of the second kind* (r.c. II.)¶. Near the plaitpoint-temperature $T_P$ the liquid

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* Kuenen, *Archives Néerl.* xxvi. pp. 378–379; Commun. No. 4; *Zeitschr. phys. Chemie*, xi. p. 44.

† Kuenen, *Archives Néerl.* xxvi. pp. 382–385; Commun. No. 4; *Zeitschr. phys. Chemie*, xi. p. 47.

‡ Commun. No. 7, p. 6.

§ Kuenen, *Archives Néerl.* xxvi. pp. 376–377, 380–382; Commun. No. 4; *Zeitschr. phys. Chemie*, xi. p. 47.

‖ In order to make the volumes in our figures decide about the situation of the phases above each other, we should take the volume of the unit of weight as the unit of volume. In doing so a phase of larger volume is a lighter phase at the same time, and will therefore appear in the upper part of the tube.

¶ Kuenen, *Archives Néerl.* xxvi. pp. 388–389; *Zeitschr. phys. Chemie*, xi. p. 45.

will be very flat and indistinct, and more so at the beginning than near the end of the condensation. Below $T_P$ the condensation is normal.

6. This second case has never been realized till now. I have been considering whether it might be, and the choice of the subject of this paper is the outcome of my reasoning. In explaining this I shall use a different graphical representation, namely the *p–t* figure. In a recent paper [*] I have deduced the general features of the *p–t* curves in the problem before us from van der Waals's theory. The figure obtained consists of (1) the two *vapour-pressure curves* of the component substances; (2) the *border-curves* [†] for the mixtures ($x$ = constant) having the form of loops; (3) the *plaitpoint-curve*, being the envelope of the border-curves and connecting the critical points of the two substances. The point of contact between a border-curve and the plaitpoint-curve corresponds to the plaitpoint P of van der Waals's surface; the critical point of contact R is the point in which the border-curve has a tangent parallel to the *p*-axis. When going along the border-curve, starting from its lower branch, we may either first reach R or P. These two cases correspond to the two cases mentioned above. If P is situated beyond R we have r.c. I. (figs. 8, 9); if R lies beyond P we have r.c. II. (fig. 10). Keeping in view the connexion between border-curve and plaitpoint-curve, the question whether the second case can be realized comes to the same as whether the plaitpoint-curve or a part of it may rise, while the border-curves are situated on its left side (fig. 10). Now it appears that there are different cases in which such a situation must occur. If the critical points of some of the mixtures lie outside the critical temperatures of the two substances, a part of the plaitpoint-curve will answer to the above postulate. But this is not a necessary condition. If the substance of the higher critical temperature has at the same time larger vapour-pressures than the substance of the lower critical temperature, the plaitpoint-curve will have the same property. This case

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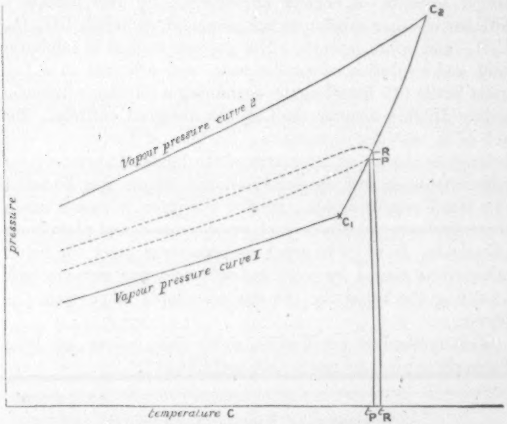
[*] Kuenen, *Kon. Akad. Amsterdam*, 29 Sept. 1894, pp. 90-99; 'Communications,' &c. No. 13.

[†] A border-curve for a mixture represents the conditions ($p$, $t$) in which it may coexist with a second phase.

is represented in fig. 1. R lies beyond P. Between the two temperatures $T_P$ and $T_R$ the mixture, the border-curve of which is drawn in the figure, must show retrograde condensation of the 2nd kind (r.c. II.). Even if the curves are more complicated than is supposed in the figure, the curve $C_1 C_2$ will nevertheless fulfil the condition at least for a part of its course.

Fig. 1.



7. There is only a small number of combinations of two substances which appear to answer the purpose. Substances of low critical temperatures mostly have high critical pressures and high vapour-pressures. When this is not so, the differences are often too small to promise striking results. My attention was at last drawn to *ethane*, a substance of low critical pressure (±50 atm.) and a critical temperature of ±34° C. Combinations of this substance with HCl, $C_2H_2$, $N_2O$, especially the last, promised good results.

For this combination I expected to find a case such as is represented in fig. 1. It will appear that my expectation has been surpassed in so far as these mixtures happen to offer some interesting properties which had never been observed and require a more complex representation than fig. 1. At the same time the phenomenon (r. c. II.), to find which was the starting-point of the investigation, has escaped observation till now.

## *Preparation of Ethane* ($C_2H_6$).

8. The ethane was prepared by electrolysis of a concentrated solution of acetate of sodium. By this process a number of other substances are generated, especially $CO_2$, $O_2$, $C_2H_4$, and some esters*. The gas was washed in sulphuric acid and a solution of caustic soda, and collected in a big glass bottle (45 litres) again containing a solution of caustic soda. In this manner the $CO_2$ was absorbed entirely. By aid of a mercury compressing machine of Cailletet, which belongs to the set of apparatus of the Leiden Laboratory for experiments at low temperatures, the ethane was liquefied in a small copper vessel. In this operation it passed again through fuming sulphuric acid, caustic potash, and phosphoric anhydride. In order to expel the permanent gases, the liquid ethane was cooled by solid carbonic acid and made to boil. In filling the tubes the gas was afterwards taken from the liquid.

This method of purification at low temperature has been formerly applied by me to $CO_2$ and $CH_3Cl$†.

## *Preparation of Nitrous Oxide* ($N_2O$).

9. This substance was taken from a commercial bottle; it was led through high-pressure tubes containing chloride of calcium and caustic potash and afterwards dried over $P_2O_5$. The purification was conducted as in the former case. During the boiling of the liquid $N_2O$ the tube could be connected with an air-pump, a sort of mercury-valve being interposed in order to prevent air from returning to the liquid.

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* Kolbe, *Lieb. Ann.* lxix. p. 279; Wiedemann, *Electricität*, ii. p. 574.

† Kuenen, *Archives Néerl.* xxvi. pp. 356, 359. Olszewski was the first to apply this method of purifying gaseous substances so far as I know.

### *Preparation of the Mixtures.*

10. The substances thus purified could be mixed in any proportion by means of my mixing apparatus, for the description of which I refer to previous investigations*. At present the whole apparatus consists of glass and copper only: the exhaustion was effected by a mercury air-pump.

### *Method of the Observations.*

11. For the observations I made use of Ducretet's apparatus†. The glass tubes in which the gases were to be compressed were connected with the above apparatus by means of ground joints, and repeatedly exhausted and filled with the gases.

12. The temperatures, all of them ranging between 0° and 40° C., were obtained by means of a continuous current of water through a tube surrounding the experimental tubes.

13. My stirring apparatus‡, which was continually used during the observations, had been slightly modified. The little piece of iron with its knobs of enamel within the high-pressure tubes was the same as before; but the electromagnet, which used to slide over the tube and accordingly within the water-vessel, had been replaced by a larger bobbin sliding over the outside of the water-vessel. In this manner the influence of the temperature of the bobbin upon the temperature of the water, the constancy of which used to be disturbed during the acting of the apparatus, was removed. The bobbin is worked by four Bunsen cells or two accumulators.

### *Results obtained with Ethane.*

14. In order to test the purity of the substances they were at first investigated separately. The gases appeared still to contain a little impurity: there was a slight increase of pressure during the process of condensation, for the ethane at 20°, 0·56 atmosphere. The amount of impurity of a gas corresponding to a definite increase of pressure at a definite temperature is difficult to decide, and entirely depends upon the substance itself and the admixture. In preparing the gas

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* Kuenen, *l. c.* p. 369. † *L. c.* pp. 357, 366. ‡ *L. c.* pp. 372 *sqq.*

a second time, the liquid ethane was cooled in liquid ethylene boiling at a low pressure (−110° C.), itself being connected with an air-pump as in the case of nitrous oxide. The ethane obtained in this manner was found to be a little purer still: the increase of pressure was 0·43 atm. at the same temperature*.

15. The critical temperature of the gases was determined very carefully: as with the mixtures, a stirring-rod had been put within the tube, and so the determination could be conducted according to the principles explained in the account of my observations with $CO_2$†. The critical temperature for the two samples of ethane amounted to 31°·95 C. and 32°·05 C. respectively. This would point to a critical temperature of ±32°·3 for pure ethane. By admitting a little air ($\frac{1}{4}$ to $\frac{1}{2}$ per cent.) into the last tube the increase of pressure at 20° C. rose to 2·7 atm., *i. e.* more than six times the former value; while the critical temperature had gone down to 31°·25 C. This would point to ±32°·2 C. as the real critical temperature of ethane. The admixture in my ethane seems to lie far below 0·1 per cent.

16. It is not impossible that, in filling the tubes, a little air remains in the gases, because they have to pass through some long tubes connected with joints before entering the experimental tube, and the air has to be expelled by means of exhaustion. I might probably have got a still purer gas by filling the tube more directly, but I preferred to apply exactly the same method which I used in preparing the mixtures, in order to be warranted against mistakes resulting from differences of purity.

17. The critical temperature of ethane as determined by former observers is somewhat higher. Dewar‡ gives 35° C., Olszewski§ 34° C., Haenlen‖ from 32° C. to 40° C., probably

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* Andrews, in his famous experiments on carbonic acid, observed an increase of pressure of more than two atmospheres in a similar case.

† Kuenen, *Kon. Akad. Amsterdam*, 29 Oct. 1893, pp. 85–90; Communications, &c., No. 8, pp. 11, 12.

‡ Dewar, Phil. Mag. [5] xviii. p. 214.

§ Olszewski, *Bulletin Ac. des Sciences de Cracovie*, 1889, p. 27.

‖ Haenlen, *Lieb. Ann.* cclxxxii. p. 245.

34°·5 C. In his experiments retardation has played an important part, and his gas cannot have been very pure; otherwise one finds a definite critical point, not a critical region as he does. He prepared the gas by the method of Gladstone, Tribe, and Frankland* from $C_2H_5I$. Olszewski obtained ethane from $C_2H_5Zn$. Both Haenlen and Olszewski purified the gas by cooling and boiling at a low temperature.

I cannot tell what the reason is of this discordance between the values for the critical temperature. Perhaps it has some connexion with the different ways of preparing the gas. I am going to repeat the experiments with ethane prepared from $C_2H_5I$. But the difference may be due to the method of determining the critical state as well. In my experiments the retardation is entirely annihilated by carefully stirring the gas, which may have lowered the critical temperature.

### *Results obtained with Nitrous Oxide.*

18. Similar results were obtained with this gas. The increase of pressure, however, was still less. At 20° C. it amounted to 0·15 atm. = 11 cm. of mercury. The impurity of the gas may be estimated below 0·0002: for the critical temperature I obtained 35°·95 and 36°·05. The true value will be 36°·1 C. probably.

19. Villard, who has prepared pure nitrous oxide by a similar process†, fixes the critical temperature of his gas at 38°·8 C. But this value was obtained by the indirect method

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* J. Chem. Soc. xlv. p. 154; xlvii. p. 236.

† Villard, *C. R.* cxviii. p. 1096; *Journal de Phys.* [3] iii. Oct. 1894. In a letter Dr. Villard tells me that his estimation of the critical temperature has been too high. In turning a tube with $N_2O$ at 36°·5 C., the liquid surface disappeared and the tube filled itself with a blue mist. Now as stirring comes to the same as repeated turning, it is quite natural that I obtained a value for the critical temperature below 36°·5 C. I have not noticed the blue mist more than 0°·2 or 0°·3 above 36°·0 C. At any rate the disagreement between Villard's result and mine has been reduced to a few tenths of a degree. But it appears from Villard's measurements of the densities of $N_2O$, that the behaviour of this substance near its critical point is less normal, so to speak, than the behaviour of carbonic acid. One feels inclined to ascribe this to the influence of minute impurities.

of measuring the densities. The liquid surface disappeared below 38° C., but he does not mention an exact value. This gas must have been very pure, judging from the regular phenomena obtained near the critical point, and the purity of the carbonic acid prepared in the same manner. Villard states that in a U-tube in which two quantities of liquid $N_2O$ were separated by a column of mercury, a pressure of a few centimetres sufficed to liquefy one of the portions completely. But this test is not so delicate as the one given above, viz. the entire increase of pressure from the beginning to the end of the liquefaction*.

20. The constancy of my results with the pure substances and the smallness of the admixture left, justify me in accepting an influence of the admixture upon the behaviour of the mixtures of a similar small amount.

### *Results obtained with the Mixtures.*

21. The number of mixtures investigated was five. The composition ($x$ parts of ethane in the volume in the gaseous state at one atmosphere) amounted to 0·18, 0·25, 0·43, 0·55, 0·76 respectively. The pressure and volume at the beginning and at the end of the condensation as observed at different temperatures are given in Tables I.–VII. The values of the volumes are only approximate. They are expressed in parts of the volume at 1 atm. and 0° C. For $N_2O$ and $C_2H_6$ only one value for the pressures has been given. Tables VIII.–X. give the volumes for the temperatures 20°, 25°, and 26° C., as determined by graphical interpolation from the values observed.

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* In filling a tube with a gas, which is compressed to a liquid afterwards, one works under unfavourable conditions for obtaining a pure substance compared to what can be obtained with liquids. The isopentane prepared by Prof. Young (Phil. Mag. [5] xxxviii. 1894, pp. 569–572) is remarkable in respect to purity. Here the increase of pressure appears to have disappeared entirely. Experiments by Battelli and others prove that even a pure liquid is not easily obtained.

## TABLES I.–VII.

### I.—$N_2O$.

| $t$. | $p$. | $v_v$. | $v_l$. |
|---|---|---|---|
| 4·8 | 35·2 | 0·0206 | 0·0022 |
| 13·3 | 43·4 | 0·0161 | |
| 19·9 | 50·8 | 0·0125 | |
| 25·4 | 57·4$^5$ | 0·0103 | 0·0027 |
| 31·5 | 65·4 | 0·0076 | 0·0031 |
| 36·0 | 71·9 | 0·0047 | |

### II.—$C_2H_6$.

| | | | |
|---|---|---|---|
| 5·85 | 27·4 | 0·0248 | 0·0033 |
| 10·65 | 30·4$^5$ | 0·0215 | 0·0034 |
| 15·4 | 33·8 | 0·0184 | 0·0036 |
| 22·4 | 39·7 | 0·0140 | 0·0038 |
| 29·35 | 45·9 | 0·0103 | 0·0046 |
| 31·0 | 47·6 | 0·0089 | 0·0049$^5$ |
| 32·0 | 48·8 | 0·0064 | |

### III.—Mixture 0·18 $C_2H_6$.

| $t$. | $p_1$. | $p_2$. | $vv$. | $v_l$. |
|---|---|---|---|---|
| 2·85 | 35·34 | 35·55 | 0·0205 | 0·0026$^5$ |
| 11·8 | 43·57 | 43·91 | 0·0143 | 0·0029 |
| 19·05 | 51·48 | 51·81 | | |
| 23·2 | 56·40 | 56·57 | 0·0094 | 0·0031 |
| 29·8 | 65·32 | | 0·0052 (?) | |

### IV.—Mixture 0·25 (?) $C_2H_6$.

| | | | | |
|---|---|---|---|---|
| 5·4 | 37·48 | 38·07 | 0·0177 | 0·0027 |
| 13·2 | 45·08 | 45·59 | 0·0131 | 0·0029 |
| 18·3 | 50·53 | 51·22 | 0·0111 | 0·0031 |
| 22·2 | 55·12 | 55·63 | 0·0094 | 0·0032 |
| 26·9 | 61·38 | 61·35 | 0·0066 | 0·0038 |
| 27·6 | 62·87 | 62·93 | 0·0065 (?) | 0·0043 |
| 28·15 | 63·36 | | 0·0046 | |

### V.—Mixture 0·43 $C_2H_6$.

| | | | | |
|---|---|---|---|---|
| 9·8 | 40·59 | ...... | 0·0150 | 0·0030 |
| 14·3 | 44·96 | 45·57 | 0·0130 | |
| 18·6 | ...... | ...... | ...... | 0·0034 |
| 20·5 | 51·75 | 52·29 | 0·0096 | 0·0035 |
| 24·6 | 56·67 | 57·01 | 0·0073 | 0·0041 |
| 26·05 | 58·42 | | 0·0055 (?) | |

Tables (*continued*).

### VI.—Mixture 0·55 $C_2H_6$.

| $t$. | $p_1$. | $p_2$. | $v_v$. | $v_l$. |
|---|---|---|---|---|
| 6·4 | 35·59 | 36·86 | 0·0195 | 0·0036 |
| 11·35 | 40·02 | 41·05 | 0·0164 | 0·0038 |
| 18·4 | 47·02 | 48·06 | 0·0126 | 0·0043 |
| 25·4 | 54·87 | 55·46 | 0·0084 | 0·0050 |
| 26·05 | 56·12 | | 0·0069 | |

### VII.—Mixture 0·76 $C_2H_6$.

| $t$. | $p_1$. | $p_2$. | $v_v$. | $v_l$. |
|---|---|---|---|---|
| 5·25 | 31·31 | 32·86 | 0·0217 | 0·0035$^5$ |
| 12·4 | 36·99 | 38·54 | 0·0173 | 0·0037$^5$ |
| 18·4 | 42·22 | 44·05 | 0·0140 | 0·0040$^5$ |
| 21·95 | 45·81 | 47·05 | 0·0118 | 0·0042$^5$ |
| 26·0 | 50·25 | 51·11 | 0·0092 | 0·0048 |
| 27·15 | 51·55 | 52·16 | 0·0083 | 0·0053 |
| 27·85 | 52·55 | | 0·0066 | |

## TABLES VIII.–X.

### VIII.—Volumes at 20° (fig. 3).

| $x$=0·0. | 0·18. | 0·25. | 0·43. | 0·55. | 0·76. | 1·0. |
|---|---|---|---|---|---|---|
| 0·0125 | 106 | 102 | 98$^5$ | 113 | 130 | 155 |
| 0·0025$^5$ | 30 | 32 | 35 | 42$^5$ | 41$^5$ | 37$^5$ |

### IX.—Volumes at 25° (fig. 4).

| $x$=0·0. | 0·18. | 0·25. | 0·43. | 0·55. | 0·76. | 1·0. |
|---|---|---|---|---|---|---|
| 0·0104$^5$ | 87 | 78 | 70$^5$ | 84$^5$ | 98$^5$ | 126 |
| 0·0026$^5$ | 33 | 35$^5$ | 42 | 48 | 45 | 40 |

### X.—Volumes at 26° (fig. 5).

| $x$=0·0. | 0·18. | 0·25. | 0·43. | 0·55. | 0·76. | 1·0. |
|---|---|---|---|---|---|---|
| 0·0101 | 85$^5$ | 73 | 58$^5$ | 69 | 92 | 99 |
| 0·0027$^5$ | 34 | 37 | 51 | 58 | 48 | 47 |

The results are laid down in fig. 2, and figs. 3, 4, and 5.

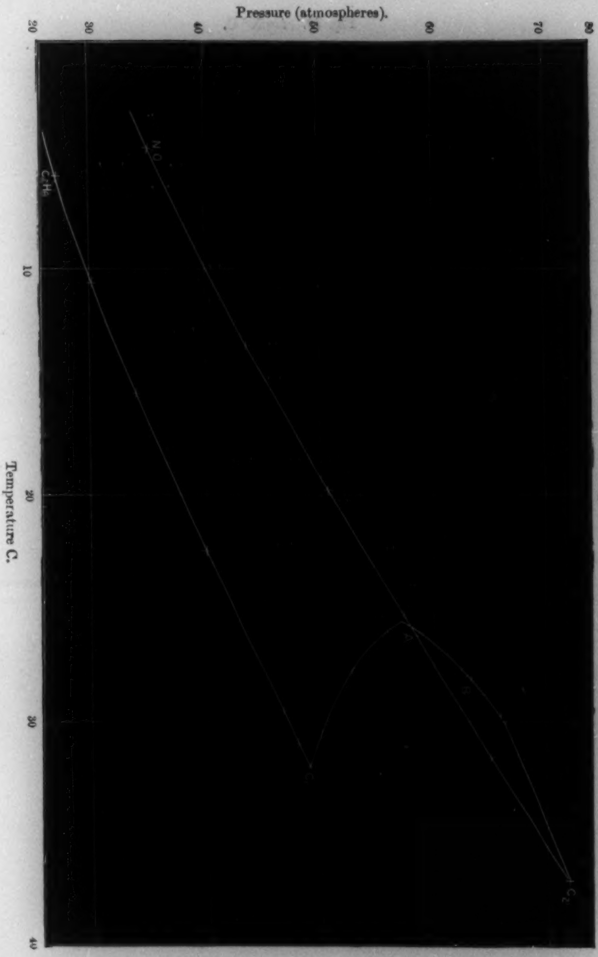
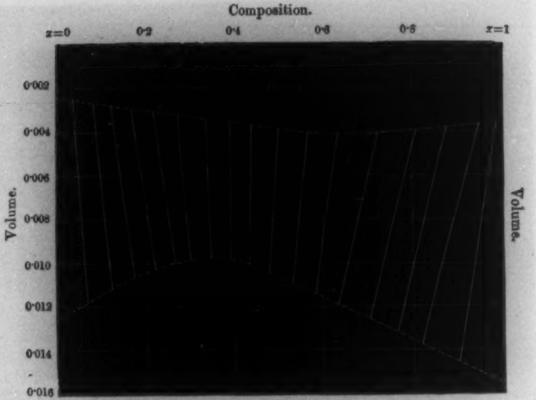

Pressure (atmospheres).
20
30
40
50
60
70
80
Temperature C.
10
20
30
40
$C_2H_6$
$N_2O$
A
B
C
$C_2$

Fig. 2.

Fig. 3*. $t=20°$ C.



* There is a mistake in fig. 3 in so far as the straight lines near about $x=0\cdot2$ should be parallel to the $\gamma$ axis, as in figs. 4 and 5.

Fig. 4. $t=25°$ C.

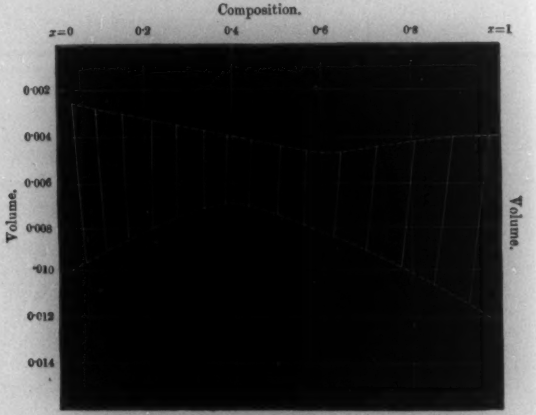
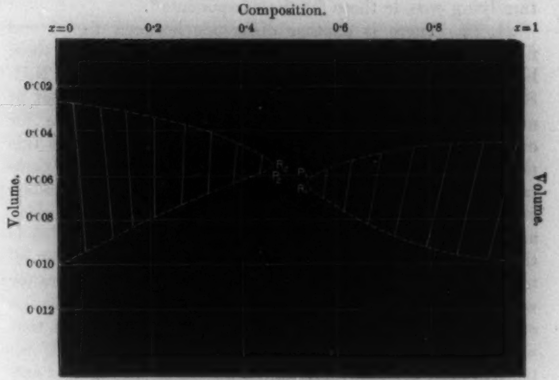


Fig. 5. $t = 26°$ C.



22. The axes of coordination in fig. 2 are $p$ and $t$. This figure may be compared with fig. 1, which represented the curves as they would have been if the phenomena had been as little complicated as possible.

The curve $C_2H_6 - C_1$ is the vapour-pressure curve for ethane, $N_2O - C_2$ the same for nitrous oxide. $C_1$ and $C_2$ are the critical points. $C_1ABC_2$ is the plaitpoint-curve. The curves of the shape of loops are border-curves for the mixtures.

23. There are two striking differences between fig. 1 and fig. 2.

(1) The critical temperatures for a part of the mixtures lie below those for the components. By adding $C_2H_6$ (32°) to $N_2O$ (36°), the critical temperature is lowered to a disproportionate extent. For a mixture containing $\pm 0{\cdot}1$ of $C_2H_6$ the critical temperature has gone down as far as to 32°, the c. t. for pure ethane. All mixtures containing more ethane than 0·1 have critical temperatures below 32°. Addition of $N_2O$ to $C_2H_6$ therefore makes the critical temperature decrease instead of increase. The lowest critical temperature ($\pm 25{\cdot}8$) belongs to a mixture containing $\pm 0{\cdot}5$ of ethane.

A case like this has never been observed till now; van der

Waals's theory shows the possibility of the critical temperature lying outside those for the components[*].

24. (2.) There is another difference between fig. 1 and fig. 2. The border-curves of the mixtures do not all of them lie between the vapour-pressure curves of $C_2H_6$ and $N_2O$. Some of them lie above the $N_2O$ curve. It follows that at every temperature there is a maximum of pressure for one of the mixtures. From the figure it appears that this maximum lies somewhere between the mixtures the composition of which is 0·18 and 0·25, say ±0·2. The border-curves of the mixtures 0·18 and 0·25 differ only very slightly and in the figure almost coincide. The meaning of this is that the maximum belongs to almost the same mixture at all temperatures represented in the figure. If the mixture for which the pressure is a maximum varied quickly with change of temperature, the border-curves of the mixtures in that neighbourhood would intersect at perceptible angles. If we tried to draw the curve giving the maximum pressure at any temperature, it would lie a very little above the border-curves for $x=0·18$ and $x=0·25$, and be about parallel to those. This curve we shall call the *maximum-curve.*

25. There is another remarkable quality of the border-curves in this region near the maximum, viz. the narrowness of the border-curves, *i.e.* the very small increase of pressure during the condensation. The value of this increase amounts to 0·2–0·3 atm. for the first mixture, which is only a very little more than what still remained in the pure nitrous oxide itself[†].

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[*] There is one instance of a mixture, the critical temperature of which lies *above* those for the components, observed by Dewar, namely, of $CO_2$ and $C_2H_2$ (Proc. Roy. Soc. of Lond. xxx. p. 543).

[†] The increases for the second mixture (0·25) are somewhat higher, viz. ±0·6 atm., which must be due to a somewhat larger impurity of that mixture. Probably the pressures of this mixture are therefore a little too high at the same time. The maximum will therefore be nearer to the first mixture (0·18). That is why I have put it equal to ±0·20. On the whole the values for the increase of pressure are a little irregular, which is quite natural considering the difficulty of these observations with mixtures. From the observations one might, perhaps, conclude that the maximum with rise of temperature shifts a little towards the $N_2O$; but as this seems rather uncertain, I prefer taking it constantly equal to 0·20.

We may therefore almost take it equal to zero. This agrees with what follows from the theory of mixtures. In a maximum-point (and also in a minimum-point) the two coexisting phases have the same composition ($x$) though different volumes ($v$), and there is no increase of pressure during the condensation. In order to determine the exact value of the maximum, a large number of mixtures lying about $x=0{\cdot}2$ should be investigated: only the small admixture in the components themselves would of course impede the fixing of the maximum-curve.

26. In itself the existence of a maximum (or minimum) pressure is not a new phenomenon. Guthrie*, Konowalow†, and others have found the same with different mixtures. Only, so far as I know, a maximum (or minimum) has never been traced up to the critical temperature. In Konowalow's mixtures the maximum appears sometimes to shift with change of temperature, and accordingly probably to disappear below the critical temperature. The above results prove that this need not be the case at all. This fact may be expressed in this manner: the maximum-curve need not reach the vapour-pressure curve of one of the substances. In my experiments it reaches the plaitpoint-curve, near B.

27. These results will be much better understood by inspecting figs. 3, 4, 5. The curves in these figures give the relation between the composition of the mixtures and the volumes at which the condensation begins and at which it ends (*vid.* § 1 *sqq.*), and may at the same time be considered as the projection of the connodal curves of the plait in van der Waals's surface upon the $v$–$x$ plane. The figures belong to the temperatures 20°, 25°, and 26° C. respectively.

28. If the phenomena were such as would correspond to fig. 1, the plait with rise of temperature would get narrower near the $C_2H_6$ plane ($x=1$). At 32° C. the curve would loose itself from the $v$-axis for $x=1$, whilst forming a plaitpoint there; above 32° C. it would withdraw towards the $N_2O$ axis ($x=0$), where it would disappear at 36° C. (critical temperature of $N_2O$).

29. However, this is not what really happens. With rise

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* Phil. Mag. [5] xviii. p. 510 *et sqq.*

† Wied. *Ann.* xiv. p. 34.

of temperature the plait becomes narrower somewhere near the middle. Consequently, at a temperature far below 32° C., near 25°·8 C., the plait divides into two parts. At that moment two plaitpoints appear ($P_1$ and $P_2$)[*]. The two parts into which the plait is divided henceforth withdraw towards $x=0$ and $x=1$ separately. At 32° C. the right-hand plait disappears at $x=1$. At 36° C. the left-hand plait disappears in $x=0$. Above 36° C. there is no plait left: the surface is convexo-convex henceforth, and all its points represent stable phases.

30. A maximum pressure (or minimum) manifests itself in the $v$-$x$ figure in the position of one of the lines connecting the pairs of coexisting phases being parallel to the $v$-axis. The lines on both sides of the maximum line will be turned in opposite directions (with a minimum the direction in which the lines turn is the opposite of what it is here). But the angles of the lines are very small in the case of $C_2H_6$ and $N_2O$. On the right-hand plait the lines differ more: the increase of pressure is accordingly larger on that side of the surface. In the figure the turning of the lines had to be exaggerated in order to show their direction.

31. The critical phenomena of the mixtures were much simpler than I expected to find them. All the mixtures showed normal condensation up to the critical point, and a difference between plaitpoint temperature and critical temperature could not be determined with any certainty. The probable cause of this disagreement I shall refer to after having deduced more completely the theoretical consequences of the experimental results laid down in fig. 2, and figs. 3, 4, 5 (*vid.* §§ 43–46).

### *Theoretical Conclusions to be drawn from the Experimental Curves.*

32. A. *Maximum-Curve.*—It may be proved that the border-curve of a mixture for which the pressure becomes a maximum

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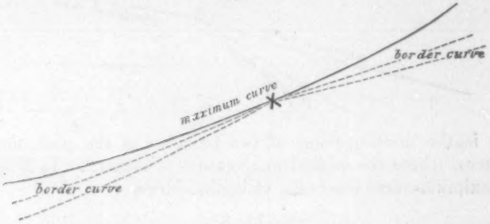
[*] In two interesting papers (Wien. *Ber.* xcviii. pp. 1154–91; *Archives Néerl.* xxiv. pp. 57–98, 295–368) Prof. Korteweg has derived the geometrical properties of the plaits and plaitpoints. The case occurring here, viz. the formation of two plaitpoints of the same kind at the same time, is discussed on pp. 303–305.

touches the maximum-curve with both its branches. This is represented in fig. 6. In every point of the maximum-curve a similar meeting of three curves takes place. If the maximum-mixture does not change much with the temperature

Fig. 6.



(as we found was the case with $C_2H_6$ and $N_2O$), the border-curve of the maximum mixture must have nearly shrunk to *one* curve coinciding with the maximum-curve.

33. Apparently the *p–t* figure is not at all convenient for showing the situation of the border-curves near the maximum-curve. The border-curves for the mixtures situated on both sides near the maximum-mixture cover each other in the figure. In a case like this it is much better to add as a third axis of coordination the *x*-axis, and to draw the *p–t*-curves for the mixtures each in its own plane. The curves together in this manner form the *p-t-x*-surface. Sections of the *p-t-x*-surface perpendicular to the *t*-axis again give curves having the shape of loops (*p–x*-curves), which may be considered as an extension of Konowalow's curves*: he only gives the upper branches of the *p–x*-curves. A complete *p–x*-curve is given by Prof. van der Waals in his treatise †.

34. The maximum-curve meets the plaitpoint-curve in B. Fig. 7 shows the manner in which the three curves (the maximum-curve and the two branches of the plaitpoint-curve) meet in B. It will have to be decided theoretically whether, perhaps, the plaitpoint curve has no singular point in B, in which case the maximum-curve would touch it in B.

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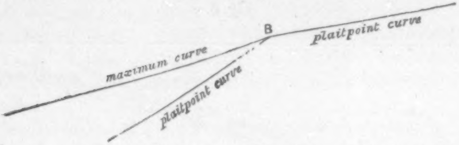
* Wied. *Ann.* xiv. p. 34.

† *Arch. Néerl.* xxiv. p. 21.

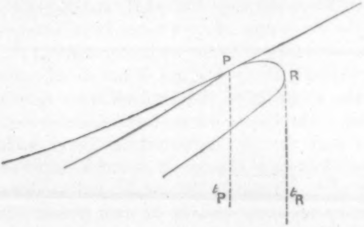
35. B. *Critical Phenomena.*—The plaitpoint-curve (fig. 2) consists of three parts, being situated between both the critical points C and $C_2$, and separated by the two points A and B.

Fig. 7.



A is the meeting-point of two branches of the plaitpoint-curve, where the critical temperature is lowest*. In B the maximum-curve meets the plaitpoint-curve.

Fig. 8.



36. In the part $C_2B$ the relative position of plaitpoint-curve and border-curves is like fig. 8. P lies in the direction we called beyond R, and the border-curves touch the plaitpoint-curve on its right side. The mixtures having their plaitpoint between $C_2$ and B, *i. e.* containing less than 0·2 $C_2H_6$,

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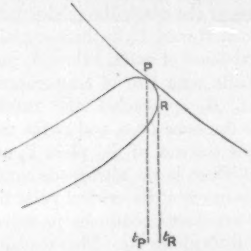
* The existence of a singular point in A was suggested to me by the experimental curves (fig. 2, *vid.* § 42). Professor van der Waals, to whom I showed my experimental results, told me that he has theoretical reasons for believing that the plaitpoint-curve is continuous during its whole course, so that neither A nor B wonld be singular points. The conclusions drawn in §§ 40–42 and figures 11 and 12 entirely depend upon the existence of a singular point in A. There is, however, no connexion between those and the rest of this paper. Professor van der Waals will publish his results ere long.

therefore must have retrograde condensation of the first kind (r.c. I.) between the temperatures $t_P$ and $t_R$.

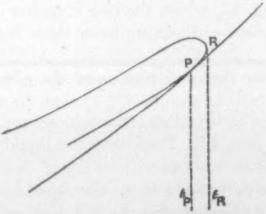
37. In the part $C_1A$ the curves are situated as in fig. 9. The border-curves lie on the left-hand side, but the plait-

Fig. 9.



point-curve falls. P lies beyond R. The mixtures having their plaitpoint here, *i.e.* containing more than 0·5 $C_2H_6$, must also have r.c. I. between $t_P$ and $t_R$.

Fig. 10.



38. The part BA, however, fulfils the condition for the existence of r.c. II., as is shown in fig. 10 (*vid.* § 6). The plaitpoint-curve rises, and the border-curves lie on its left side. R lies beyond P. In this region lie the mixtures the composition of which is between 0·2 and 0·5 $C_2H_6$.

In consequence of the complexity of the curves as compared to fig. 1, the region of r.c. II. is a great deal smaller than it would have been according to fig. 1 (BA instead of $C_1C_2$). It is easy to see that this was the only thing which could happen: r.c. II. could not disappear entirely.

39. These rather strange conclusions are entirely made clear by figs. 3, 4, 5. These represent exactly the same phenomena, only in a different manner. If P lies above R we have r.c. I.; if it lies below R, we have r.c. II. At first, after the dividing of the plait, the plaitpoints $P_1$ and $P_2$ lie on opposite sides of $R_1$ and $R_2$ in the two plaits. This corresponds to the existence of r.c. I. below A, and r.c. II. above A in fig. 2. While with rise of temperature the plait $P_2R_2$ shrinks together, $R_2$ approaches the maximum-line. $P_2$ approaches $R_2$ at the same time, and at the moment that the maximum reaches the end of the plait, $P_2$ and $R_2$ coincide. At that moment there is no retrograde condensation. The mixture $x=0{\cdot}2$ behaves at its critical point like a pure substance. $P_2$, however, now continues to move upwards, and henceforth lies a little above $R_2$. That explains the existence of r.c. I. between B and $C_2$. If there had not been a maximum, r.c. II. would have existed all the way from A to $C_2$.

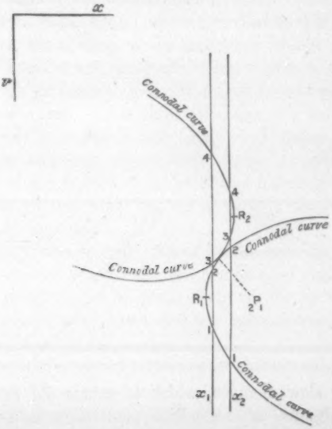
40. The critical phenomena near the point where the plait divides into its two branches ($t=25{\cdot}8$, $p=57{\cdot}7$ atm.) are of a rather complex nature. This will be understood by the contemplation of fig. 11, where the two branches of the connodal curve at the moment of parting have been drawn on a much larger scale.

Let us consider the condensation of the mixtures $x_1$ and $x_2$ separately. It will be seen (*vid.* § 1) that the mixture $x_1$ in 1 begins to show a liquid phase which increases, decreases, and disappears in 2 (r.c. I.). Then, in 3, the liquid appears again, and in 4 the whole mixture will be liquid (normal condensation). Mixture $x_2$ liquefies in 1: the liquefaction is at an end in 2 (normal condensation): in 3 a vapour phase appears which disappears in 4 (r.c. II.).

41. Quite close to this temperature (below and above it) similar complicated phenomena will exist. A little above 25·8 there are even some mixtures which show first r.c. I. and then r.c. II. successively with compression. But as soon as the plaits have moved so far that there is no $x$-line cutting both plaits, the critical phenomena become the ordinary phenomena for a mixture (r.c. I. or II.).

42. The $p$–$t$-curves in the neighbourhood of A have a more complicated character, corresponding to the behaviour of the plait (fig. 12). The two branches of the experimental plaitpoint-curve meet in a singular point. The border-curves show a doubling, which disappears at a small distance from A. A fuller explanation of the figure seems hardly necessary. For clearness' sake only two border-curves have been drawn in the figure on an exaggerated scale.

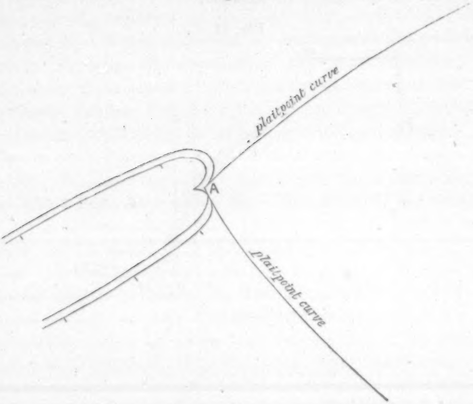
Fig. 11.



43. How is it that in my experiments the mixtures did not show any of those critical phenomena partly of a so complicated nature, and almost behaved like pure substances near their critical points? (§ 31). The reason lies at hand : I have pointed out the smallness of the increase of pressure, *i.e.* the approximate parallelism of the straight lines in fig. 3 (§ 30), and the exceeding narrowness of the loops (border-curves) in fig. 2 (§ 25). Accordingly, as will be noticed in both figs. 2 and 5, the two critical points P and R lie close together, and the distance between the temperatures of the plaitpoint and the critical point of contact ($t_P$ and $t_R$), for the same mixture,

can be very small only. An estimation from the original figure 2 gives $\pm 0^{\circ}{\cdot}1$ C. at the utmost for the distance between $t_P$ and $t_R$, and in some parts of the plaitpoint-curve—for instance near B—much less still. Now in order to fix so small a difference the temperature ought to be perfectly constant for a long while, which was not the case in my water-vessel.

Fig. 12.



There were slow changes, which of course did not prevent the determination of the critical point taken as a whole. I think this circumstance may be taken as a sufficient explanation of the disagreement between theory and experiments.

44. However, there is another cause which must have cooperated in confusing the pure phenomena, viz. the influence of gravitation. It was Gouy[*] who, in the case of pure substances, first pointed out the importance of this factor near the critical point, where the substances become so highly compressible. In the case of mixtures the influence of gravitation is not of a quite simple nature. The result is this :

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[*] *Compt. Rend.* cxv. p. 720, cxvi. p. 1289; *cf.* Kuenen, 'Communications, etc.' No. 8, p. 10.

near the plaitpoint there is a small region in which the complete process of the condensation is confused; namely in this manner, that with compression at a certain moment the liquid surface between the phases disappears at some distance from the ends of the tube. In this manner the process of retrograde condensation is cut off halfway; and if the distance between the two critical temperatures is very small, the phenomenon may perhaps disappear entirely*. This suggests the use of horizontal, or at least nearly horizontal, tubes for experiments on the critical phenomena.

45. Now in this region, where gravitation plays an important part, the stirring of the substance cannot be of any avail; on the contrary, the equilibrium, which is very much influenced by gravitation, is spoilt rather by mixing together the different layers. So in this region the only thing we can do is, to wait a long time, and Gouy's experiments with an almost pure substance show that "long" means "days" here; and of course that would be no use unless the temperature and the volume could be kept absolutely constant, which is practically impossible.

46. Though the special critical phenomena predicted by means of van der Waals's theory have escaped observation so far, there is no reason to doubt their reality or to see any contradiction between them and my experimental results, I believe.

47. Some of the results arrived at in this investigation may be enumerated here once more:—

1. The mixtures of $C_2H_6$ and $N_2O$ containing more than 0·1 of $C_2H_6$ have critical temperatures lying beneath those of the substances (§ 23).

2. The pressures of the mixtures lie partly above those of $N_2O$, and accordingly show a maximum situated near 0·2 $C_2H_6$ (§ 24).

3. The maximum does not disappear with increase of temperature, but remains up to the critical region: the maximum-curve reaches the plaitpoint-curve (§ 26).

4. The mixtures ranging between 0·2 and 0·5 $C_2H_6$ have r.c. II., the rest r.c. I.

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* Kuenen, *Verslagen kon. Akad. Amsterdam*, 25 Mei, 1895.

I intend now to investigate mixtures of acetylene and carbonic acid, a group of which according to Dewar[*] has critical temperatures lying above those of the components. If I should be able to confirm this result, I shall treat that combination in the same manner experimentally and theoretically as I have done the combination of $C_2H_6$ and $HN_2O$ in this paper.

The experiments described in this paper have been carried out in the Physical Laboratory at Leiden, to the Director of which, Professor Kamerlingh Onnes, I am indebted for continuous and invaluable advice and help.

## DISCUSSION.

Prof. CAREY FOSTER and Prof. RAMSAY complimented the author on the very lucid way he had expounded a by no means easy subject.

Dr. SIDNEY YOUNG congratulated the author on the able use he had made of his lucky discovery of two bodies such that their mixture should have a lower critical temperature than that of either of the pure substances. Prof. Ramsay and he (Dr. Young) had made experiments on the vapour-pressure of mixtures of alcohol and ether, and had found great difficulty in preventing the separation of the components when the volume was altered, and he could therefore thoroughly appreciate the utility of the author's device for overcoming this difficulty. They had also experienced considerable difficulty in filling the tube with a mixture of known composition and free from air, and he considered that when dealing with mixtures it was better to employ gases, although they could not be obtained in so perfect a state of purity as liquids, on account of the greater ease with which a mixture of known composition can be obtained. The plan of making separate observations on the pure substances was a good one, and, considering that the author measures the increase of pressure during the process of condensation, so that any air which happens to be present produces the maximum effect, the small rise in pressure obtained indicated a high degree of purity in the gases employed. He would like to ask the author if, in the case of mixtures, he found it possible to determine accurately the point where condensation commenced and ended, for with the alcohol and ether mixtures they found it very difficult to determine these points. He also hoped the author would continue his observations in the direction indicated in the paper.

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[*] Proc. Roy. Soc. of Lond. xxx. p. 543.

Mr. INWARDS suggested that, in the case of liquids which act on iron, the iron stirrer could be enclosed in glass or india-rubber. It might also be possible to obtain more efficient stirring by means of a small fan or propeller worked by an electro-magnet rotating outside the tube.

Dr. KUENEN, in his reply, said that, when the mixtures were well stirred, the pressures at which condensation commenced and ended were well marked.

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## XLVII. *An Electromagnetic Effect.* *By* F. W. BOWDEN*.

SOME time ago, under the direction of Prof. Perry, I was making some experiments suggested by Dr. Larmor. The following curious observations were made, and as Dr. Larmor thinks them distinct from his own object, I beg leave to bring them before the notice of the Physical Society. In fig. 1, N and S are nearly cubical blocks of iron whose edges are about 6 centim. long, forming the poles of an electromagnet. The field between N and S near the middle was about 1100 C.G.S. A is the end view of a glass tube, 4 millim. internal diameter and about 30 centim. long, containing mercury and connecting two large mercury troughs, and a current of about 40 amperes was sent through it. A stand-pipe, B, 2 millim. diameter, indicated the pressure of the mercury. When the current passes in one direction (out from the paper) the mercury rises 15 millim. in B. When the current is reversed, the mercury falls 15 millim. Reversing the magnetic field produces the same effect as reversing the current.

With the tube in the position shown in fig. 2, the effects were of the same kind but not so marked, the rise and depression being about 10 millim. As the tube was lifted more and more out of the field, the effects became less and less.

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* Read June 28, 1895.

The field being vertical as in fig. 3, the mercury *rose* in the stand-pipe when the current passed, and in whatever direction the current passed; reversing the current did not reverse the pressure-effect produced. Also reversing the field did not reverse the pressure-effect produced.

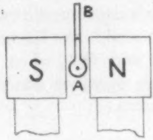

Fig. 1.

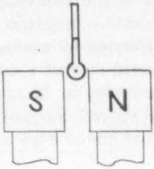

Fig. 2.

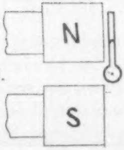

Fig. 3.

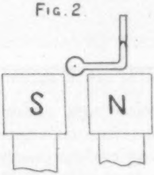

Fig 4

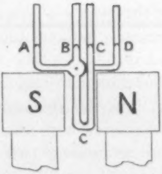

Fig 5.

I again used a horizontal field as in fig. 4, the stand-pipe showing now the side-pressure in the tube parallel to the field. It was my intention to let fig. 4 really represent fig. 3 turned through a right angle, and again the mercury always rose in the stand-pipe, whatever the direction of the current or field.

Lastly, I let four stand-pipes communicate with the middle of the tube. The current passing in one direction, the mercury in B rose, in C fell, and in A and D rose only momentarily during the starting of the current. When the current was reversed, the mercury in B fell and in C rose, and rose momentarily in A and D.

The non-reversible effects of figs. 3, 4, and in the tubes A and D of fig. 5 are probably due to curious motions of the mercury, but it seems difficult to understand how. They do not occur when the tube is far away from the magnetic field.

## Discussion.

Prof. S. P. **Thompson** said that there appeared to be three unexplained effects—one proportional to the current and the field, and reversible ; another, independent of the direction of the current or of the field ; and a third, which only occurred while the current was changing in strength. In addition there may be a fourth effect, which up to now has not been noticed. The motion of the mercury column in fig. 1 was in the opposite direction to that of the drag on a conductor carrying the current. An apparent rise in pressure might be due to a decrease in the density of the mercury due to the heat developed by the current.

Mr. **Blakesley** asked if the author had noticed any changes in level in the mercury reservoirs at the ends of the tube.

The Author, in his reply, said the reservoirs at the ends were so large that no changes of level were appreciable.

## XLVIII. *The Electrical Properties of Selenium.*

*By* SHELFORD BIDWELL, *M.A., F.R.S.*[*]

### § 1. *Preliminary*[†].

SELENIUM, which is supposed to be an elementary substance, is capable of existing in several distinct modifications. The amorphous variety consists either of a finely divided red powder, or of a vitreous mass which resembles black glass in appearance and does not conduct electricity. Amorphous selenium melts at about 100° C., but at temperatures between 100° and 217° the black semi-liquid mass gradually hardens into a grey metallic-looking solid. This consists of Se in the crystalline form: it melts at 217°, and is a moderate conductor of electricity, its conductivity being temporarily increased by the action of light. This peculiar influence of light upon Se has attracted much attention, and below is given a list of published papers relating to the subject[‡].

### § 2. *Selenium Cells.*

Any device consisting essentially of a mass of crystalline selenium in combination with two metallic electrodes, and so arranged as to expose a relatively large surface for light to act upon is commonly, but not very appropriately, termed a "Selenium Cell." So many inquiries have reached me as to the construction of the sensitive cells which I have at different times exhibited before this Society and elsewhere, that I venture to think a short account of the process may be usefully given here.

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[*] Read June 28, 1895.

[†] A summary of the principal results will be found at the end of the paper.

[‡] Willoughby Smith, Journ. Soc. Tel. Eng. ii. p. 31; Earl of Rosse, Phil. Mag. March 1874, p. 161; Sale, Proc. Roy. Soc. 1873, p. 283; Phil. Mag. March 1874; Werner Siemens, Phil. Mag. November 1875, p. 416; Draper and Moss, 'Chemical News,' xxxiii. p. 1; Moss, Proc. Roy. Soc. May 11, 1876; Adams and Day, Proc. Roy. Soc. 1876, p. 113; Phil. Trans. 1877, p. 313; C. W. Siemens, Proc. Roy. Inst. 1876, p. 68; Sabine, Phil. Mag. June 1878, p. 401; Graham Bell, 'Nature,' xxii. p. 500; Proc. Nat. Acad. Sci. April 1881; Shelford Bidwell, Phil. Mag. April 1881, January 1883, August 1885, March 1891; Fritts, 'Electrical Review,' March 7, 1885, p. 208; Minchin, Phil. Mag. March 1891, p. 207.

A slip of mica about 55 millim. long, 17 millim. wide, and 0·4 millim. thick, is sandwiched between two semi-cylinders of boxwood about 18 millim. in diameter and of somewhat greater length than the mica, the ends being held together by screws. The whole is smoothed down in a lathe until the edges of the mica are flush with the surface of the wood. A screw of 16 threads to the centim. (40 to the inch) is cut upon the middle portion of the cylinder for a length of 45 centim. The mica is then removed from the wood, and two small holes are drilled near each of its ends. An annealed copper wire 0·19 millim. in diameter (No. 36 s.w.g.) is tightly wound around the notched portion of the mica, the turns being made to occupy alternate notches, and its ends are secured by passing them through two of the drilled holes. A second wire is then wound into the other notches, its turns alternating with those of the first. These wires constitute the electrodes, and great care is taken that they do not touch each other at any point.

The next step is to apply the selenium. A brass plate 2 millim. thick is supported upon an iron tripod and covered with a sheet of thin mica; upon this is laid the prepared mica slip, small weights being placed upon its ends to steady it. The surface of the wired portion of the slip is evenly covered with 1 gramme (or a little less) of powdered vitreous selenium, and a small Bunsen burner is lighted beneath the brass plate. In a few minutes the greater part of the Se will melt: some of it, however, will probably crystallize, forming hard grey lumps, and when this occurs the heat must be continued, and if necessary increased, until all the grey lumps have disappeared. Then the Se is worked smoothly and uniformly over the slip with a steel spatula, particular care being taken that the surface is covered quite up to the edges. This operation is often found a troublesome one, but if the temperature be properly regulated, there is little difficulty about it. When the temperature is too low, hard crystalline lumps are formed; when it is too high, surface-tension causes the selenium to gather up into drops, and it becomes as impossible to spread as if it were mercury. The Bunsen flame should be adjusted so that the temperature is only just above the melting-point, 217°; the selenium then assumes a plastic semi-fluid condition and can be easily manipulated.

When a satisfactory surface has been secured, the cell is immediately removed by means of forceps and placed upon a thick copper plate to cool quickly. The Se surface should at this stage be black and lustrous, and the resistance between the electrodes sensibly infinite.

The Bunsen flame having been turned down sufficiently to lower the temperature to about 120°, the cell is replaced upon the hot plate. In a few minutes parts of its bright surface become dimmed, and shortly afterwards the whole turns a dull grey colour. The temperature is then cautiously raised until signs of melting just begin to appear, generally near one of the edges. When this occurs the burner is instantly withdrawn and the flame slightly lowered. The darkened spot recrystallizes in the course of a few seconds, and the burner is then replaced and left for four or five hours, during which time the temperature of the Se should be only a few degrees below the melting-point. Another hour is occupied in slowly cooling the cell, the flame being gradually lowered and finally extinguished. This process of long heating and slow cooling is generally spoken of as "annealing."

The resistance of such a cell as that described is generally from 50,000 to 100,000 ohms in the dark, and 50 or 60 per cent. less in diffused daylight. If alternately screened and exposed, it will with an electromotive force of 50 volts or upwards easily actuate an ordinary telegraph relay.

### § 3. *Hypothesis as to the Action of Light upon Selenium.*

Selenium as supplied commercially is never free from impurities, and indeed I have lately been informed by a distinguished chemist, who has given some attention to the subject, that perfectly pure selenium has not yet been obtained. Graham Bell states that the samples collected by him in different parts of the world were found to contain, among other things, the metals lead, iron, and arsenic.

Ten years ago I suggested * that metallic selenides, whether originally existing as impurities in the Se or formed at the expense of the electrodes during the process of "annealing," might play a very important part, not only in relation to the conductivity of crystalline Se, but also in bringing about the apparent change of its resistance under the influence of light. According to my hypothesis, the conductivity of Se depended mainly upon the selenides which it contained. I supposed the conduction to be of a truly electrolytic character, the current decomposing the selenides, and depositing upon the anode amorphous Se and upon the kathode the various metals. Amorphous Se is a non-conductor: unless, therefore, the deposited Se combined more or less freely with the metal of the anode, forming upon it a layer of conducting selenide, the resistance of a Se cell would, under the influence of a current, soon rise to infinity. It has been shown that Se does slowly unite with at all events some metals when merely brought into contact with them, and I ventured to suggest that light played its part in reducing the resistance by facilitating this union. The action would occur not only at the anode, but throughout the body of the Se, the recombination of the separated molecules of Se and the metal (forming the "Grotthuss chain") being similarly assisted.

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* Proc. Phys. Soc. vol. vii. p. 129; Phil. Mag. August 1885, p. 178.

This hypothesis would, as I showed, explain many observed facts which could not otherwise be readily accounted for, and I adduced in support of it several arguments which need not here be repeated. But the hypothesis postulated two important assumptions which I was not able at the time (nor when I returned to the subject five years later) to justify by experimental evidence. It assumed that solid metallic selenides conduct electrolytically, and that the combination of selenium with a metal is accelerated by the action of light.

My recent experiments, some of which are discussed in the present paper, were undertaken primarily with the object of testing these two assumptions. In the course of the investigation, however, many other interesting points presented themselves for consideration, and some of the results arrived at are also here recorded. The experiments are described in the order which appeared to be most convenient; it is of course not that in which they were actually performed.

## § 4. *The Effect of Annealing upon the Specific Resistance of Crystalline Selenium.*

The resistance of Se which has been crystallized and annealed out of contact with any metal appears to be always much greater than when metallic electrodes have been fused into it in the usual fashion. It also depends to a large extent, and in a manner which is not yet fully explained, upon the treatment which the Se has received.

*Exp.* 1.—A number of disks were prepared by casting Se in a mould formed by placing a glass ring, such as is used for microscope slides, upon a glass plate. The thickness of a disk was made approximately uniform, and its surfaces polished by rubbing upon fine glass-paper laid upon a sheet of plate glass. The disk to be tested was inserted between pads of vulcanized rubber covered with tinfoil, which constituted the electrodes, and the whole was placed between hinged boards and loaded with a weight of 28 lbs. (12·7 kilos). It is unnecessary to describe the tests in detail, inasmuch as the only result arrived at was the negative one that crystalline Se has no definite specific resistance. In different tests of disks prepared from the same sample and as far as possible in the same manner, it varied from 33 megohms to 1630.

The specific resistance is certainly not always diminished, as is generally believed, by prolonged heating at a high temperature; *i. e.* between 200° and 217°. It is indeed often increased after such an operation, as in the following extreme instance.

*Exp.* 2.—A disk of Se was crystallized and heated for an unrecorded number of hours in a copper air-bath at about 200°. Its specific resistance was afterwards found to be 38·5 megohms. It was again heated at the same temperature for three hours. When cold its specific resistance was 660 megohms. In both cases it was cooled slowly.

## § 5. *Action of Selenides.*

On the other hand, prolonged heating always diminishes the resistance of a Se "cell" having electrodes fused into it. This I have attributed to the action of the conducting metallic selenide which would be formed during the heating at the expense of the wires.

*Exp.* 3.—For the purpose of testing this conjecture, a number of cells were constructed of Se having incorporated with it cuprous selenide in different proportions. The wire used was platinum ; it was of the same gauge in all cases (0·27 millim.), and the number of turns per unit of length was also the same (10 per centim.). The surface area, however, varied somewhat, and in order to facilitate comparison the figures, as given in the annexed table, express in each case the resistance of a square centim. of surface. The light employed was always, except where otherwise stated, that derived from an 8 candle-power incandescent lamp, the filament of which was 1 ft. (about 30 centim.) distant from the face of the cell. None of the cells containing added selenide were annealed, but were cooled as soon as the Se had crystallized. That in which there was no $Cu_2Se$ was annealed for six hours. For comparison, the table is headed with particulars of a good ordinary copper-wire cell of similar dimensions.

Table I.

| Composition of Cell. | Annealed or Unannealed. | Percentage of added $Cu_2Se$. | Resistance in dark of 1 sq. cm. Megohms. | Percentage decrease in light. |
|---|---|---|---|---|
| Cu Wire and Se ......... | Well annealed | 0 | 0·7 | 45 to 50 |
| Pt Wire and Se ......... | ,, ,, | 0 | 13·9 | 33 |
| Pt wire and $Se+Cu_2Se$ | Unannealed. | 0·5 | 12·0 | 32 |
| ,, ,, | ,, | 1·5 | 14·7 | 57 |
| ,, ,, | ,, | 3 | 3·6 | 47 |
| ,, ,, | ,, | 4 | 0·90 | 38 |
| ,, ,, | ,, | 5 | 0·25 | 28 |

In the cell containing 1·5 per cent. of $Cu_2Se$, the thickness of the Se coating was accidentally made much less than the diameter of the wires, instead of equal to it, as in the other cells : hence its unduly high apparent resistance and its correspondingly great sensitiveness (for its exposed surface was disproportionately great). In other cases the results are as regular as could be expected. They demonstrate clearly enough that a cell of fairly good sensitiveness and conductivity may be formed without any annealing, if a suitable quantity of metallic selenide be first added to the Se. They also render very evident the fact that an excessive quantity of selenide, while it reduces the resistance to a comparatively low point, only does so at the cost of the sensitiveness. This agrees with the well-known fact that an ordinary Se cell whose resistance has been unduly lowered by too long heating is only moderately sensitive to light. Exactly what part is played by the free selenium remains yet to be determined; it is certain that cuprous selenide by itself is quite insensible.

### § 6. *Sensitizing Insensitive Selenium.*

During the last fifteen years I have worked with a great many different samples of Se, and have observed that they did not all possess exactly the same degree of sensitiveness: some were better than others, but the sensitiveness of the best was probably not more than 8 or 10 per cent. greater than that of the worst. Lately, however, I have been supplied commercially with a batch of selenium which, under the usual treatment, is almost absolutely insensitive to light. This Se differs a little in appearance from the ordinary article. In the vitreous condition its colour is of a lighter shade, and its surface is less lustrous than usual. When melted (above 217°) it forms a tenacious semi-fluid mass, which adheres like treacle to the mica and spatula and is difficult to spread; it does not exhibit the capillary effects previously referred to, and at a suitable temperature it crystallizes with great rapidity. It has not been analysed, but such impurities as it may contain probably do not include the metallic selenides commonly met with*.

*Exp.* 4.—Three copper-wire cells of the usual size were made with this Se and annealed for several hours. Their resistances in the dark had the abnormally high values of 170,000, 290,000, and 520,000 ohms respectively, the last named being very thinly coated. When illuminated by the incandescent lamp at 12 inches, the decrease of the resistance amounted in the case of the first two to only a fraction of 1 per cent. (instead of the customary 40 or 50 per cent.), and in the thinly-coated cell to about 6 per cent.

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* Two other samples of insensitive Se have since been supplied to me from different sources.—*June* 28th.

*Exp.* 5.—Two perfectly similar copper-wire cells of smaller size were coated, one with the insensitive Se and the other with ordinary Se, and annealed side by side for 5½ hours. On subsequently testing, the resistance of the ordinary cell was found to be 20,500 ohms in the dark and 40 per cent. less when illuminated, while that of the other was 780,000 in the dark and only 2·5 per cent. less under illumination.

*Exp.* 6.—A cell was constructed having exactly the same dimensions as those last mentioned, and was coated with insensitive Se with which 3 per cent. of cuprous selenide had been previously incorporated. It was not annealed, but cooled gradually during about fifteen minutes. Next day its resistance in the dark was 190,000 ohms, and when illuminated by the lamp, 140,000, the decrease being 26 per cent.; in sunlight it fell to 43,000 ohms, or 77 per cent. less than in darkness.

*Exp.* 7.—Another cell of the same size was made in which 5 per cent. of selenide was added to the insensitive Se. Its resistance in the dark was 105,000 ohms, and when illuminated by the lamp 79,000, a fall of 25 per cent.

*Exp.* 8.—Another similarly sized cell had 3 per cent. of *lead* selenide mixed with the Se. Its resistance dark was 363,000 ohms, and illuminated 10½ per cent. less.

It appears, therefore, that the addition of a small quantity of cuprous selenide imparts a fair degree of sensitiveness to the anomalous Se, at the same time bringing down its resistance to nearly the normal value. An equal proportion of lead selenide produces a similar, though less marked effect. It would be interesting to try selenides of arsenic and other metals, but I have not yet had time to do so.

It is certain that an ordinary well "annealed" Se cell with copper electrodes contains a relatively large quantity of copper selenide. Mr. W. Hibbert was kind enough to analyse the Se taken from one of my old cells to which no foreign substance had been intentionally added, and found that it contained 2·28 per cent. of combined copper, equivalent to 3·71 per cent. of cuprous selenide. Of course this must have been derived mainly from the copper electrodes.

### § 7. *Effect of Time.*

The fact that the resistance of crystalline Se with metallic electrodes fused into it decreases very greatly in course of time was first noticed by Prof. W. G. Adams and Mr. R. E. Day[*], who thought that it was due to the Se having become more completely annealed. In a former paper[†] I have suggested that the decrease is more probably to be attributed to the short-circuiting of the cell by an excessive amount of conducting selenide, formed by the gradual union of the Se with the metal of the electrodes. This view receives strong support from the following observations.

*Exp.* 9.—In the year 1891 I constructed a copper-wire cell but did not crystallize nor anneal the Se, which remained therefore in the vitreous state: its resistance was sensibly infinite. The cell was laid aside in a box until March 1895, when it was tested and its resistance found to have fallen to about 8 ohms. The cell was quite unchanged in appearance, the selenium surface being perfectly black and glossy. The decrease of resistance could not possibly be accounted for by spontaneous crystallization, and could hardly have been due to any other cause than the formation of selenide in the interior. The cell was unfortunately destroyed before it occurred to me to use it for an experiment like the following.

*Exp.* 10.—A cell made in 1881 had then a resistance of about 100,000 ohms and was very sensitive to light. In 1895 its resistance had fallen to 10 ohms and it was quite insensitive. This was connected with a storage-battery of 26 cells, a detector-galvanometer being included in the circuit. When the current was turned on, the galvanometer-needle underwent a momentary strong deflexion and immediately returned to zero. The dark resistance of the cell was then found to have risen to 60,000 ohms, and it was once more sensitive to light. Clearly a short circuit caused by the selenide had been burnt out.

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[*] Phil. Trans. vol. clxvii. pt. i. p. 348.

[†] Phil. Mag. March 1891, p. 250.

### § 8. *Action of Light in promoting the Formation of Selenides.*

Several attempts to ascertain whether the union of Se with a metal was assisted by illumination resulted indecisively. The following simple experiments are however, I think, fairly conclusive.

*Exp.* 11.—One side of a thick plate of copper was evenly coated with red amorphous Se by causing the fumes of boiling Se to play upon it. Half the plate was then covered and the other half exposed, first to diffused daylight and afterwards to sunlight. In diffused daylight the exposed half was perceptibly darkened in the course of two or three hours; in sunlight it quickly assumed a dark chocolate colour, the screened portion remaining bright red.

*Exp.* 12.—Two pieces of mica were similarly treated, but the exposed portions were not perceptibly darkened by prolonged exposure to sunlight. They became, however, covered with a slight "bloom," like that seen on a ripe plum, which I am inclined to attribute to the formation of an oxide.

*Exp.* 13.—A brass plate coated with red Se was exposed to sunlight in a photographic printing-frame under a design cut out of black paper and intended to represent a butterfly. A perfectly sharp and intense print of the design was produced upon the red Se. This was made on April 17 last: it has since been kept in the dark and is now exhibited to the Society.

The chocolate colour is closely matched by that of a mixture of red precipitated Se and cuprous selenide in about equal parts.

### § 9. *The Effect of Temperature upon the Resistance of Crystalline Selenium.*

Text-books and dictionaries of chemistry appear to be about equally divided upon the question whether the resistance of crystalline Se is increased or diminished by rise of temperature. There are high authorities for both opinions. In a paper published in 1883[*] I gave an account of some experiments which indicated that the resistance of Se, "or rather perhaps of selenium cells," as I was careful to add, became a maximum at a certain temperature, which varied a little with different specimens but was generally a few degrees higher than the average temperature of the air. Eight different cells were tested, showing well-defined maxima at temperatures of 13°, 14°, 22°, 23°, 23°, 24°, 25°, and 30° respectively.

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[*] Phil. Mag. Jan. 1883, p. 31.

On further investigating the subject I have traced this curious effect to the action of the fused-in electrodes. So far as I know from a great number of experiments, a piece of crystalline Se into which wires have been fused *always* acquires a maximum resistance at a certain temperature. On the other hand, the resistance of a piece having external electrodes pressed into contact with it is *always* diminished by a rise of temperature.

*Exp.* 14.—A rectangular plate of Se was cast in one of the white-glazed earthenware "pans" in which moist water-colours are sold. Two platinum wires were made red-hot, and their ends embedded along the shorter sides of the rectangular plate a little below the surface. The plate was then crystallized and annealed and its surfaces smoothed with glass-paper.

The plate was suspended inside an air-bath, the bulb of a thermometer being in contact with it, and the resistance between the platinum-wire electrodes was taken at temperatures ranging from −2° to 12°. The results, which are given in the second column of Table II., indicate that the resistance was greatest when the temperature was 6°.

The same plate was then placed between two pads of india-rubber covered with tinfoil which served as electrodes, and were pressed into good contact by a weight of 500 grammes. The arrangement was placed in the air-bath, and the resistance between the opposite faces of the plate observed at various temperatures. As is shown in the third column of Table II., the resistance diminished steadily as the temperature rose.

TABLE II.

| Temperature. Degrees C. | Resistance between Electrodes fused into ends. Megohms. | Resistance between Electrodes pressed against surface. Megohms. |
|---|---|---|
| −2 | 45·6 | |
| 0 | 48·7 | |
| 2 | 52·0 | 38·5 |
| 4 | 52·3 | 36·8 |
| 6 | 53·3* | 34·0 |
| 8 | 52·5 | 30·2 |
| 10 | 49·6 | 26·6 |
| 12 | 46·7 | 23·9 |

* Maximum.

Thus with rising temperature the resistance of the *same* piece of Se appears to reach a maximum when measured between fused-in wires, and to decrease *ab initio* when measured between electrodes which are pressed upon its surface.

Beyond doubt the resistance of the Se really falls in both cases. The apparent preliminary rise when the electrodes are fused in, is due to the unequal heat expansion of the Se and of the metal. The coefficient of linear expansion of Se is twice as great as that of copper and three times as great as that of platinum. The effect of heating is to loosen the tight grip of the Se upon the metal and so to increase the resistance of the junction. The rate at which this junction-resistance increases is at first greater than that at which the specific resistance of the Se diminishes: soon, however, the latter effect predominates, and thus the resistance of the combination of Se and a metal passes a maximum.

## § 10. *Porosity of Crystalline Selenium.*

The consideration of certain phenomena, which will be referred to later, led me to believe that crystalline Se, notwithstanding its metallic appearance, must be a sensibly porous substance. Experiments were made with the view of ascertaining whether this was the fact.

*Exp.* 15.—One end of a brass tube was closed by a polished disk of crystalline selenium, 11·2 millim. in diameter and 1·25 millim. thick, which was tightly fixed by an indiarubber collar: to the other end was attached a glass tube which terminated in an open point about 3 millim. in diameter. The whole of the indiarubber and the edges of the Se disk were thickly coated with shellac varnish. The closed end of the tube was dipped into water and air was forced into the open end. No bubbles were formed upon the Se: if therefore Se be porous its pores must be very small.

*Exp.* 16.—A transpiration experiment was then made. The tube was fixed in an upright position with the Se disk at the top and the glass point at the bottom, the latter dipping into a basin of water. A wide-mouthed glass bottle was supported mouth downwards over the tube, enclosing its upper end. Coal-gas was slowly admitted into the bottle from a small nozzle. The indiarubber tube conveying the gas was for seven feet (about 2 metres) of its length coiled up in a vessel of cold water. When the gas was first admitted water rose for a short distance inside the glass tube owing to the cooling effect of the refrigerated gas: but after a minute or two it began to descend again, and soon air-bubbles were slowly but regularly given off at the pointed end. This continued until the bottle of gas was removed, when the bubbles at once ceased and the water again began to rise in the tube.

Crystalline Se is therefore sensibly porous, and no doubt absorbs moisture from the air.

### § 11. *The Polarization of Selenium by Currents.*

Among the many remarkable properties of Se which were first observed by Prof. W. G. Adams and Mr. R. E. Day in their well-known research, is the power it possesses of setting up a secondary or polarization current after being disconnected from a battery. As all who have worked much with Se must know, the opposing and ever varying electromotive force of polarization renders it very troublesome to make accurate resistance tests by the ordinary bridge method. Unless it is worth while to expend a considerable amount of time, one has to be contented with two or at most three significant figures, and even this degree of accuracy cannot be attained unless care is taken to depress the battery and galvanometer keys only for a moment*.

In a former communication I stated my belief that these polarization effects resulted from the electrolysis of the metallic selenides contained as impurities in the Se. Whether this be so or not, the following experiments plainly indicate that the presence of moisture is necessary for the production of the phenomenon.

*Exp.* 17.—The electrodes of a Se cell were connected first with the poles of a battery, and then by means of a "change-over" switch with a galvanometer: this produced a deflexion of 90 divisions, indicating an E.M.F. of rather more than $\frac{1}{100}$ volt. The cell was then placed in a glass receiver over strong sulphuric acid, the connecting wires being passed through an indiarubber stopper. From time to time it was successively joined to the battery and the galvanometer, and the polarization current was observed to be gradually diminishing. After 18 hours the deflexion was only 3 divisions. The air was then exhausted from the receiver, and 24 hours later no polarization current whatever could be detected, even after prolonged connexion with the battery. A current greater than $\frac{1}{300}$ part of that which occurred in ordinary air would certainly not have escaped observation.

*Exp.* 18.—The cell was afterwards suspended for an hour in a receiver over a basin of water and then tested for polarization. The spot of light was immediately deflected far beyond the limits of the scale.

Probably therefore the polarization results merely from the electrolysis of water; in any case the presence of water seems to be requisite for its production.

It is perhaps worth noting that little if any polarization is exhibited by crystalline Se of the coarsely granular form obtained by gradually *lowering* the temperature of the molten substance, instead of by heating solid vitreous Se. The specific resistance of this form is much lower than that of the other, and its sensitiveness is also less.

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* If the battery key be kept down for a few seconds, and after it is raised the galvanometer key be depressed, a considerable deflexion due to the secondary current will generally be observed. For exact measurements it is necessary to balance to a constantly changing false zero.

### § 12. *The Effect of Moisture upon Conductivity and Sensitiveness.*

The water ordinarily present in Se, even if it had no other effect, would naturally influence its apparent conductivity by acting as a shunt or alternative path for the passage of the current. We should expect, therefore, that if a cell were made as dry as possible, its resistance would be increased, and this was found to be the case.

*Exp.* 19.—A cell with a Se surface measuring 4 centim. by 1·5 centim., and containing 64 turns of 0·19 millim. copper wire, was suspended in a receiver over sulphuric acid, and tests were made of its resistance both in darkness and under illumination by an 8 candle-power lamp at 30 centim. The results are given in Table III.

TABLE III.

Selenium Cell in Receiver over $H_2SO_4$.

| Time. Hours. | Resistance. Dark. | Resistance. Illuminated. | Percentage Decrease. |
|---|---|---|---|
| 0 | 50,400 | 25,400 | 49·5 |
| 28 | 83,000 | 35,500 | 57·2 |

The dark resistance of the cell, it will be seen, increased in 28 hours from 50,400 to 83,000 ohms: if, therefore, the water which it originally contained acted like a metallic shunt, its resistance taken alone must have been about 128,000 ohms. Now it was found that a thin plate of Se, after having been dried over sulphuric acid for 22 hours, lost $\frac{1}{2800}$ part of its weight. The weight of the Se in the cell used in the present experiment was about 0·4 gramme; probably, therefore, it originally contained about $\frac{1}{7000}$ gramme of water. Knowing the dimensions of the cell (which are given above), it is easily calculated that if this quantity of water when uniformly distributed between the electrodes of the cell offered a resistance of 128,000 ohms, its specific resistance must have been approximately 7800 ohms. This is of the same order of magnitude as the specific resistance of good distilled water, though that of purer water is of course much higher. We may fairly conclude, then, that absorbed moisture plays no active part in diminishing the dark resistance of Se, but behaves merely as if it were an inert shunt.

As regards *sensitiveness*, moisture might conceivably exert one of four different influences. If it acted simply as a shunt, its removal ought to increase the sensitiveness of the cell in an easily calculable degree. If its presence were essential to the chemical or physical change which is effected by the agency of light, then a perfectly dry cell would also be perfectly insensitive. If moisture, without being indispensable, were yet in some degree favourable to the operation of light, the sensitiveness of the cell, though it might possibly be increased when the water was withdrawn, would still not be so great as if a metallic shunt of equal resistance had been cut out. Lastly, if the influence of water were positively prejudicial, its removal would result in a greater increase of sensitiveness than if it had been a mere shunt.

The figures in Table III. seem to show that the presence of water, though not essential to sensitiveness, does to some extent assist the action of light. The percentage decrease of the resistance of the dried Se under illumination is considerably greater than that of the undried, but still it is not so great as it would have been if a shunt of 128,000 ohms (the resistance of the water alone) had been withdrawn. In the latter case the resistance of the dry cell in the light would have been only 31,700 ohms instead of 35,000, and the percentage decrease 61·8 instead of 57·2.

*Exp.* 20.—Three cells were at different times constructed, and after being kept for some hours at a temperature of about 200° were without any previous cooling transferred as rapidly as possible to the sulphuric acid receiver. All turned out to be sensitive to light while in the dry air. Unless, therefore, Se can condense moisture in its pores at a temperature of 200°, which is not probable, its sensitiveness to light is not entirely dependent upon the presence of water. Having regard to the observations detailed in the next section this was contrary to my expectation.

### § 13. *Attempted Electrolysis of Metallic Selenide.*

Many abortive attempts were made to ascertain whether cuprous selenide conducts electricity entirely like a metal, as is generally believed, or like an electrolyte, as required by my hypothesis. The experiments of which an account is given in this section appear to show that if the conduction is not altogether electrolytic, it is under certain conditions, at least partly so. It must, however, be admitted that the results, though of considerable interest, cannot be regarded as conclusive. The condition requisite for apparent electrolysis is that the surface of the selenide should be moist, a condition of course suggestive of some secondary action.

*Exp.* 21.—A mass of cuprous selenide about 2 millim. in thickness was placed between two platinum foil electrodes, each of which was covered with four layers of filter-paper moistened with distilled water. The arrangement was pressed together by a weight of 28 lbs. (12·7 kilos), ordinary precautions being taken to avoid short-circuiting. A current averaging 0·03 ampere was passed through the moist selenide for about four hours. On examining the papers afterwards, it was found that those which had been in immediate contact with the selenide were stained a dark grey colour, due evidently only to transferred particles of selenide. The other papers had received stains which differed greatly in appearance according as they were upon the anode or the kathode.

On the *anode* papers the stains were scarlet, and I satisfied myself that they were beyond doubt due to red amorphous Se. For (1) stains of a precisely similar hue and character were obtained by electrolysing a solution of selenious oxide contained in a pad of filter-paper, though of course in this case the stain appeared upon the kathode. (2) The stains turned dark brown when heated. (3) They were not affected by cold hydrochloric acid, as red oxide of copper would have been. (4) Nor by sulphuric acid. (5) Nor (unless very slowly) by cold nitric acid. (6) Hot nitric acid quickly dissipated them. (7) So also did a mixture of cold nitric and hydrochloric acids. (8) The red stuff could be volatilized at a temperature below that at which the paper was scorched.

On the *kathode* papers the stains were of a dark brown, nearly black, shade, surrounded by small irregular patches of green, blue, and orange. The dark-brown stuff acquired a metallic copper-coloured lustre when burnished, which is sufficient proof that it consisted, largely at all events, of finely divided metallic copper. It was ascertained that if a little of the selenide itself were finely powdered, rubbed into moist paper and dried, no such metallic appearance was produced by burnishing.

The experiment was repeated several times with variations in the details : *e. g.* in one case the selenide was fused with an excess of Se, in another with an excess of Cu. But it was invariably found that red stains were formed at the anode, and almost invariably traces of metallic copper appeared at the kathode.

This experiment naturally led me to try to obtain electrically liberated selenium in larger and measurable quantities.

*Exp.* 22.—Some selenide of copper was prepared by heating together 126 parts of shredded copper-foil and 79 of crushed Se in a closed crucible to bright redness. The product was an iron-grey, cindery-looking mass.

A fragment of this was held in a brass clip, and the lower portion of it dipped into a beaker of water opposite a strip of Pt foil. The selenide was joined to the negative pole of the battery, the Pt to the positive : thus the water was made the anode in relation to the selenide. A current of 0·025 ampere was passed for half an hour. In a few minutes after starting, the water had become scarlet and quite opaque with suspended red Se. Unfortunately, however, the selenide was very friable, and numerous small particles were detached from its surface by the hydrogen bubbles which formed upon it ; these became mixed with the liberated Se and made it impossible to ascertain the weight of the latter.

*Exp.* 23.—In order to obtain a more coherent substance, two parts of Se were thoroughly incorporated with one of $Cu_2Se$ ; the mixture was then fused in an earthenware mould, and thus formed into a rectangular plate weighing 1·0731 gramme. Se itself being a very bad conductor, it was believed that practically the whole conduction would take place through the selenide. The plate was immersed in water with a strip of Pt, and a current averaging 0·023 ampere was passed for ten minutes. As soon as the circuit was closed the black plate began to give off dense red clouds; and when it was dried and weighed after the experiment, it was found to have lost 0·0250 gramme. If the decomposition had been primarily electrolytic, the weight of liberated Se, assuming its electrochemical equivalent to be 0·00082 *, would have been no more than about half that amount, namely 0·0113 gramme. The red Se was filtered out of the water and examined for particles of *débris.* None were detected by the unassisted eye, but under the microscope many became visible, though whether in sufficient quantity to account for the observed excess of weight is somewhat doubtful.

*Exp.* 24.—This was a repetition of the last, except that the plate contained six parts of Se to one of $Cu_2Se$ (instead of two to one) and weighed 1·0223 gramme. The current, which averaged 0·016 ampere, was left on for 30 minutes. The actual loss of weight was 0·0386 gramme; the calculated loss, according to the electrolytic law, being 0·0236 gramme. In this case, therefore, with a weaker current and a less friable mixture, the observed exceeded the calculated loss by only 64 per cent. instead of 121 per cent. as in the previous instance. The microscope again revealed the presence of numerous small black particles. The closer approximation is in favour of the possibility that the excess might have been due to the disruption of fragments of the selenide. Further experiments, which need not be detailed, leave the point still doubtful.

This effect of electrical action may be exhibited in a striking manner as follows:—A sheet of moistened filter-paper is laid upon a metallic plate, preferably of Pt, which is in connexion with the positive terminal of a 50-volt battery; a pencil formed of one part of $Cu_2Se$ and six parts of Se is connected by a flexible wire to the negative terminal. When this black pencil is drawn over the paper, it makes a bright red mark which is immediately broken off if the current is interrupted or reversed. If a copper plate be used, the marks will be brown instead of red.

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* The electrochemical equivalent of hydrogen multiplied by the atomic weight of Se $=0·000010384 \times 79 = 0·000820336$. Quite possibly, however, the E.C.E. of Se is only half this value.

The red stuff separated in the foregoing experiments turned black when heated, and fused and crystallized like ordinary Se. The resistance of a small cell made from a portion of it was 65 per cent. lower than the average; the cell was very sensitive to light, the diminution of its resistance under illumination being 53 per cent.

The question naturally presented itself, whether the separation of the red Se might not in some not easily imagined manner be due to the hydrogen liberated from the water, and not primarily to the current.

*Exp.* 25.—To test this a zinc wire 1·7 millim. in diameter was coated with a fused mixture of Se and $Cu_2Se$ and immersed in dilute sulphuric acid. The acid penetrated the pores of the coating, and soon small bubbles of hydrogen began to rise from the surface, continuing for about 5 hours. The coating was then broken up, and it was found that all the zinc inside it had been dissolved. A microscopic examination of the fragments failed to disclose the smallest trace of any red Se.

The experiment was repeated with the substitution of ordinary commercial Se, and the same negative result was arrived at. It was ascertained that sulphuric acid did not dissolve the red stuff.

*Exp.* 26.—An experiment was arranged with the view of determining whether the current exerted any action, real or apparent, upon Se itself when unmixed with any metallic selenide except such as it might contain as an accidental impurity.

A well-annealed plate of crystalline Se having a Pt electrode fused into one edge was supported in water, the electrode being about 5 millim. above the surface. A slip of Pt foil was also immersed, and the two were joined respectively to the terminals of a storage-battery of 26 cells. Until the current had been passing for more than 24 hours, there was no perceptible discoloration of the water. Shortly afterwards it was found that the plate was surrounded by a slight red deposit just above the water-line, and that the lower part of the water had become pink. On examination, it appeared that the red stuff proceeded entirely from a small hole in the plate above the water-line : the Se was therefore broken up and the course of the hole, which was full of water, was traced and found to terminate very near the Pt electrode, where no doubt platinous selenide existed.

This experiment, though not conclusive, tends to show that Se unmixed with selenide is not acted upon by the current. It is possible that moist crystalline Se may be converted into the red amorphous form by electrical action, but the question cannot be definitely settled until perfectly pure Se is obtainable.

### § 14. *Photoelectric Currents.*

Another of the interesting discoveries of Adams and Day was the fact that an electromotive force could be set up, and a current started in annealed Se merely by the action of light*. This observation has been fully confirmed by subsequent experimenters, and the belief has been expressed that the phenomenon affords an example of the direct conversion of the energy of light into that of electricity. Others have held the opinion that the effect is of a purely thermoelectric nature. My own investigations have led me to the following conclusions :—

(1) The effect is undoubtedly due to light and not to heat; or, more accurately, it is brought about by the action of radiation, and not by change of temperature.

(2) The energy of the photo-electric current is primarily of chemical or voltaic origin, and is not derived from radiation. Light merely has the effect of facilitating the chemical process, and can have no further influence when the supply of unused material is exhausted.

*Exp.* 27.—A rectangular plate of Se measuring 14 × 11 × 2 millim. had Pt wire electrodes fused into its two ends and was "annealed" for several hours. The electrodes being connected with a galvanometer, a piece of magnesium ribbon was burnt near the Se : a deflexion immediately occurred showing a current which ceased as soon as the light was extinguished. By screening the two ends alternately, it was ascertained that the effect was produced only at one junction, the other being quite insensitive. (It may happen in different cases that both junctions are sensitive or neither. As will be shown later, sensitiveness points to imperfect electrical contact between the Se and Pt due perhaps to a film of red Se.) The direction of the current through the sensitive end was from Se to Pt.

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* *L. c.* p. 333.

The Se plate was afterwards placed under a glass receiver with a basin of water, and connected with the galvanometer by wires passing through a caoutchouc stopper. In a minute or so a small current was indicated which, after slowly increasing for about 15 minutes, became constant. While magnesium was being burnt near the receiver, the strength of the current was greatly intensified; even diffused daylight temporarily increased the deflexion to the extent of 150 scale-divisions. The direction of the current was as before from Se to Pt.

The plate was then enclosed in a receiver over sulphuric acid. In 8 minutes the permanent current had completely disappeared, and exposure to diffused daylight caused a deflexion of only 2 divisions. In 20 minutes burning magnesium at a distance of 6 inches failed to produce any effect whatever. The Se had completely lost its power of generating a current under the influence of light.

The natural inference seems to be that Se (or Se containing selenide) is slowly oxidized by water, and that the oxidation is increased by the action of light*. Some points bearing on the question will be further considered in the next section.

## §15. *The Thermoelectric Quality of Annealed Selenium.*

Adams and Day believed they had obtained evidence that the thermo-electric quality of crystalline Se was altered by prolonged annealing. To use the old-fashioned terminology, they thought that by the process of annealing Se was raised from its place at the bottom of the thermo-electric series, which the experiments of Matthiessen had assigned to it, to a position somewhere above that of platinum. In other words, if a Se–Pt junction were heated to a temperature slightly above that of the other junctions in the circuit (the latter being at the ordinary temperature of the air), then, if the Se were crystallized but not thoroughly annealed, there would be a current from Pt to Se through the heated junction, but if the Se were well annealed the thermo-current would be in the reverse direction—from Se to Pt.

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* Later experiments render this doubtful. With Se which does not contain any considerable admixture of $Pt_2Se$ (and perhaps it should be added, which has not been previously used as an anode) the photo-electromotive force appears to be always in the *opposite* direction—from Pt to Se. And this seems to be the case not only with water as the electrolyte, but also with the other badly conducting liquids, such as œnanthol, used by Prof. Minchin.—*June* 28th.

They applied heat at a junction by directing upon it a blast of hot air from a glass tube terminating in a fine nozzle, the tube being heated over one or more Bunsen burners. Where it was possible, heat was also applied by holding the junction of Pt and Se between the finger and thumb. All the pieces of Se with which they worked had had Pt wires fused into their ends before being annealed.

The following experiments point to a conclusion different from that of Adams and Day.

*Exp.* 28.—Experiments were made with three different specimens of Se, all of which had been annealed for many hours. None of these had electrodes fused into them. The arrangements were varied in details, and the Pt-Se junctions heated in different ways. In all cases the direction of the thermo-electromotive force was from Pt to Se across the hot junction. The direction of the current was not affected by the addition of platinous selenide to the Se.

Further experiments were made with the Se plate referred to in the preceding section which had Pt wires fused into its ends.

*Exp.* 29.—The Pt wires being connected with the galvanometer, it was found that when one junction was touched with the finger there was as usual a current from Pt to Se, but that when the other was touched (that which had generated the photo-electric currents in a former experiment) there followed a current in the opposite direction—from Se to Pt.

All the following observations were made with this anomalous junction.

*Exp.* 30.—The junction was heated by touching it first with the pointed tip of a warmed glass rod and afterwards with a hot copper wire. In both cases there resulted a current in the *normal* direction—Pt to Se.

*Exp.* 31.—A bent glass tube having a fine nozzle at one end was heated over a Bunsen flame, and air was blown through it from the mouth upon the junction. Result, an *abnormal* current—Se to Pt.

*Exp.* 32.—The last experiment was repeated, but the air was driven through the tube by a foot-blower. Result, *normal*—Pt to Se.

*Exp.* 33.—The tube was allowed to cool, and when quite cold air from the lungs was again blown through it. Result, a current from Se to Pt stronger than that obtained with the hot blast in Exp. 31.

*Exp.* 34.—A small piece of sponge moistened with tepid water was held upon the end of a wire near the junction but not touching it. There immediately followed a small current from Se to Pt.

In short, the anomalous current from Se to Pt was in every case clearly started, not by heat but by moisture.

The succeeding experiments indicate that at the anomalous junction the electrical contact between the Pt and Se was imperfect, and that the Se contained a certain amount of platinous selenide.

*Exp.* 35.—One part of platinous selenide having been incorporated with six parts of Se, the mixture was fused and crystallized. Thus was obtained a button of crystalline Se containing about 15 per cent. of platinous selenide. The button and a piece of Pt foil were partly immersed in water and their dry ends connected to the galvanometer. A voltaic current was indicated from the button to Pt through the water.

*Exp.* 36.—The button was dried and tested for a thermo-current with Pt. Result, current from Pt to button through the junction. The button, therefore, behaved thermo-electrically like ordinary Se.

*Exp.* 37.—By means of an adjustable spring a strip of Pt foil was arranged so as to press lightly on the button. The two were connected with the galvanometer.

Touching the button near the junction with a hot wire caused a current from Pt to button.

Holding the tip of the finger very near the junction without actual contact caused a current from button to Pt.

Blowing air upon the junction from a hot glass tube produced a current from Pt to button when the air-blast was derived from a foot-blower, and from button to Pt when air from the lungs was blown through the hot tube.

Thus all the thermo-effects of the "anomalous" junction were completely imitated. Perhaps in the case of that junction good contact was prevented by a film of non-conducting red Se, or possibly the wire electrode may have been simply loose.

These effects could not be produced when using a button which consisted of Se annealed without contact with a metal and containing no added selenide, the voltaic effect being then similar in direction to the heat-effect.

## *Summary.*

1. The conductivity of crystalline Se appears to depend principally upon the impurities which it contains in the form of metallic selenides. It is suggested that the selenides conduct electrolytically, and that the influence of light in increasing the conductivity is to be attributed to its property of facilitating the combination of selenium with metals in contact with it.

2. The specific resistance of crystalline Se has no definite value but is always very high, varying in the specimens tested from about 30 to 1600 megohms. It is not in general diminished by prolonged heating unless the Se is in contact with a metal (Exps. 1, 2).

3. A Se cell having Pt electrodes and made with Se to which about 3 per cent. of cuprous selenide has been added, is, even though unannealed, greatly superior both in conductivity and sensitiveness to a similar cell made with ordinary Se and annealed for several hours. It is not, however, quite equal to a cell prepared in the usual way with copper electrodes (Exp. 3).

4. A particular sample of commercial Se which, when treated in the ordinary manner, was almost absolutely insen-

sitive to light, was rendered sensitive by the addition of a little metallic selenide (Exps. 4–8).

5. The great fall of resistance exhibited by pieces of Se with fused-in electrodes after the lapse of a few years, is not due to any material lowering of the specific resistance of the Se, but to short-circuiting by selenide formed at the expense of the electrodes. The resistance of an old cell was instantly raised from 10 ohms to 60,000 by connecting it with a 52-volt battery and thus burning out the short circuit (Exps. 9, 10).

6. Red Se in contact with copper or brass is quickly darkened by the action of light, owing, it is suggested, to the formation of selenide. Photographs may be printed on copper or brass coated with red Se and preserved in darkness for a long time (Exps. 11–13).

7. The resistance of crystalline Se always decreases with rise of temperature. The apparent increase of resistance on heating generally observed when the electrodes are fused into the substance, is to be explained by the fact that the heat-expansion of the Se is much greater than that of the metallic electrodes; imperfect contact is consequently produced at the junction (Exp. 14).

8. Crystalline selenium is porous and absorbs moisture from the air (Exps. 15, 16).

9. The polarization of Se after being traversed by a current is due to absorbed moisture (Exps. 17, 18).

10. The moisture ordinarily present in Se renders the apparent resistance much lower than the true resistance of the substance (Exp. 19).

11. The presence of moisture is not essential to sensitiveness, but appears to be in a slight degree favourable to it (Exps. 19, 20).

12. When a current is passed through cuprous selenide between platinum electrodes which are covered with moistened paper, red Se is deposited on the anode paper and metallic copper on the kathode paper (Exp. 21).

13. If cuprous selenide is made the kathode and a strip of Pt the anode in water, red Se mixed with detached particles of the selenide is deposited in the water (Exp. 22).

14. With a mixture of cuprous selenide and Se the quantity of detached black particles is greatly diminished, but the weight

of the separated red Se appears to be greater than that required by the law of electrolytic decomposition. Possibly the current has the effect of converting pure crystalline Se when moistened into the red amorphous variety (Exps. 23, 24).

15. The hydrogen produced by the action of zinc upon dilute sulphuric acid has no effect upon the cuprous selenide nor upon Se in contact with the zinc (Exps. 25, 26).

16. The photo-electric currents sometimes set up when light falls upon Se are dependent upon the presence of moisture and are no doubt of voltaic or chemical origin. (Exp. 27).

17. Experiments which have seemed to place well-annealed selenium above platinum in the thermo-electric series were vitiated by the presence of moisture. Dry Se is always below Pt (Exps. 28–37).

## DISCUSSION.

Prof. **MINCHIN** suggested that the selenium "cell" should be called a selenium "resistance." A grid having one terminal made of aluminium and the other of copper might form a true cell, and might generate an E.M.F. when light fell on it. He would like to know if the author had tried any such cell in which light, simply and solely, generated an E.M.F. He could not agree that chemical action must necessarily follow the action of light in a cell. For take the case of the oldest photo-electric cell—the thermopile,—what chemical action can we show here for all the energy of the incident heat? Chemical action due to light may or may not occur, according to the nature of the cell.

Mr. **APPLEYARD** asked whether the author had submitted these selenium resistances to the action of electric oscillations. Prof. Minchin's "impulsion" cells were greatly influenced by electric oscillations. The great variation in the resistance with time of the author's cells pointed rather to an effect of contact between the selenium and the electrodes than to an elementary change in the structure or composition. He (Mr. Appleyard) had recently tried to crystallise a supersaturated solution of sodium sulphate by electric oscillations, as well as by direct sparks, and by currents of several ampères; but no crystals could be induced to form. Change of contact rather than change of structure appeared to him to be the most promising direction in which to look for an adequate theory of selenium resistances.

Prof. RAMSAY said the quantity of the Se liberated in the electrolytic experiment was much too great to be accounted for by oxygen dissolved in the water. The study of selenium was very interesting, for this substance was on the borderland between those bodies in which the electric conduction was metallic and those in which it was known to be electrolytic.

The AUTHOR, in his reply, said he agreed that the name "selenium cell" was not an appropriate one. He had not tried the effect of electric oscillations.

## XLIX. *The Measurement of Cyclically Varying Temperature.*

*By* HENRY F. W. BURSTALL, *M.A.*, *A.M.I.C.E.*[*]

[Plates X. & XI.]

I HAVE been engaged since the latter end of 1892 in attempting the measurement of the temperatures reached in the cylinder of a gas-engine, and the following paper embodies the results which I have obtained.

So far as I am aware no experiments on this subject have been previously published; such attempts as have been made have failed from the want of a sufficiently sensitive thermometer. The platinum resistance-thermometer has, however, proved to have the required sensitiveness, and I shall devote this paper to the description of one of its forms which I have found suitable for the measurement of cyclically varying temperature.

The direct determination of the temperature in the cylinder clears the field for more complete discussion of the theory of the gas-engine, but as I would rather treat the experiments which I have already made as preliminary only, I will not enter into any discussion on this point in the present paper.

I had hoped during this work to have had the collaboration of Prof. Kapper, but unfortunately, owing to the pressure of other work, he was unable to devote the necessary time to these researches. I wish to take this opportunity of thanking him for putting at my disposal the experimental gas-engine at King's College, and also for many valuable suggestions he has made during the course of the work.

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[*] Read May 24 and June 14, 1895.

The engine used is an Otto cycle-engine. This cycle, which is that now most generally used in internal combustion-engines, is completed in four strokes of the piston.

During the first stroke a charge of mixed air and combustible gas is drawn into the cylinder by the forward motion of the piston, the air- and gas-valves are now closed automatically, and the piston, on its second stroke, compresses the mixture, nearly adiabatically *, into the clearance space. This space forms a prolongation of the working cylinder, and has a capacity of about 45 per cent. of the volume swept through by the piston. The pressure reached at the end of the compression stroke is thus about four atmospheres. At the commencement of the third stroke communication is opened to the ignition-tube; the mixture then explodes, and the pressure rises to about fifteen atmospheres. The piston moves forward and the pressure falls, as the heated gases expand, until it is about three and a half atmospheres. This takes place just before the end of the stroke, and at this point the exhaust-valve opens. During the fourth stroke the products are discharged from the cylinder.

In order to measure the extremely high temperatures which were known certainly to be reached during such a cycle, some special form of thermometer had to be employed: not only is the temperature high, but the pressures to be dealt with are such as to destroy any thermometer not constructed of materials capable of resisting great mechanical stresses. It appeared to me that the platinum resistance-thermometer, which has been brought to such perfection by Callendar and Griffiths, and whose constants can be determined with such a high degree of accuracy, gave the greatest promise of success.

The general form and construction of such thermometers

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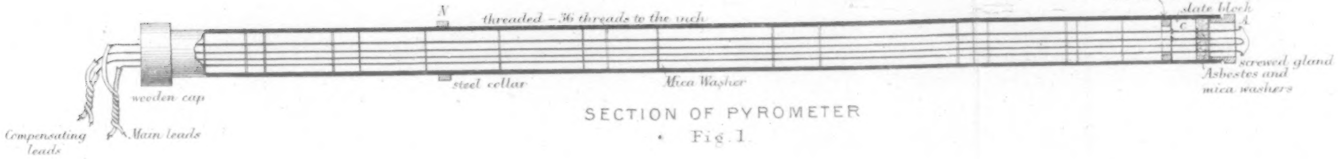
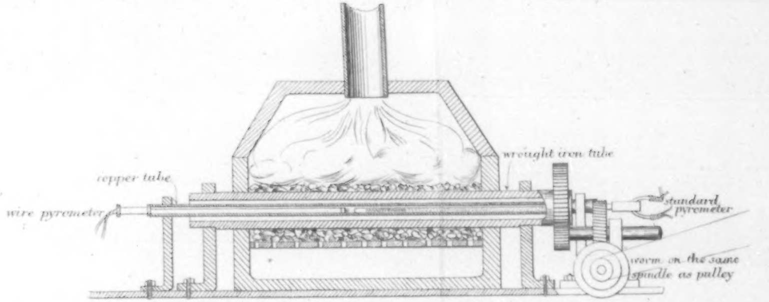
* During compression the pressure and volume are approximately connected by the relation $pv^{1\cdot3}=\text{constant}$.


N
threaded – 36 threads to the inch
Steel collar screwed in slate block
C
A
wooden cap
steel collar
Mica Washer
screwed gland
Asbestos and mica washers
Compensating leads
Main leads

SECTION OF PYROMETER
Fig. 1.

END VIEW.



SECTION OF TUBE FURNACE SHOWING PYROMETERS IN POSITION.
Fig. 4.

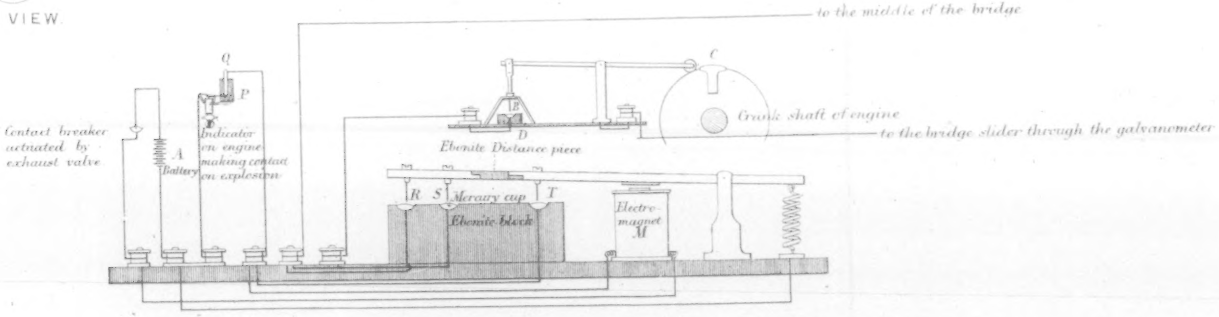

to the middle of the bridge
Q
P
C
B
D
Crank shaft of engine
to the bridge slider through the galvanometer
Contact breaker actuated by exhaust valve
A
Battery
Indicator on engine making contact on explosion
Ebonite Distance piece
R
S
Mercury cup
T
Ebonite block
Electro-magnet
M

DIAGRAM SHOWING CONNECTIONS FOR CLOSING GALVANOMETER CIRCUIT.
Fig. 3.

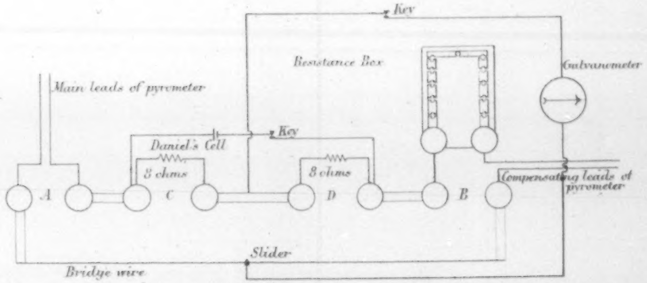


DIAGRAM OF BRIDGE CONNECTIONS
Fig. 2.

Mintern Bros. lith.

are now so well known, that I will only describe the special form which I have employed to fulfil the following conditions, which had to be satisfied in this particular case :—

(i.) The thermal capacity must be small, as the variations of temperature are extremely rapid. A whole stroke of this engine is completed in less than one fourth of a second ; during this time the temperature varies about 500° C., and as the temperature has to be measured at any fraction of the stroke, a lag of 0·01 second corresponds to one tenth of the stroke of the piston.

(ii.) The body of the thermometer must be made of some strong material such as iron or steel, as the impulsive pressures would immediately destroy any weaker material.

(iii.) From the nature of the thermometer chosen, the leads must be well insulated from each other and from the body of the instrument, the insulating material being such as to stand high temperatures.

To fulfil all these conditions was by no means easy. In order to satisfy the first I was forced to employ a naked wire of small diameter, which obviously gives the minimum thermal capacity per unit of surface. I was fully aware that the whole of Callendar and Griffiths's work had been done on wires which were carefully shielded from the least contamination by means of an outer envelope; hence it might have been expected that a naked wire would prove unreliable, but I show later that, provided suitable precautions are taken, naked wires give satisfactory results, at any rate to the order of accuracy of my experiments.

The difficulties of obtaining the requisite mechanical strength, and at the same time good insulation, were very great; and nearly twelve months' work was expended before a satisfactory solution of the problem was obtained. The greater number of the earlier instruments were deficient in mechanical strength. In most laboratory experiments this is seldom of great importance ; but this weakness invariably led to the thermometer being blown out of the engine after a few explosions, and the results were disastrous to the experiments.

### *Description of the Thermometer.* (Plate X. fig. 1.)

The body of the thermometer consists of a seamless steel tube 15 inches long and $\frac{3}{4}$ inch outside diameter; the outside of the tube is screwed from end to end with a fine thread. Working on this thread is a nut N, so arranged that the thermometer-wire can be immersed to any required depth in the gas-engine cylinder. For a distance of about one inch from one end, A, the tube is threaded in the interior and a small ring screwed in. Against this ring, which forms an internal collar, rests a circular slate block (C) pierced with four small holes through which the four leads pass. These leads are of platinum, 0·03 inch diameter and 4 inches long. About 1·5 inches from the end A small platinum collars are gold-soldered on to the leads; these prevent the leads from being blown out of the tube, by bearing against the slate block. In the stem of the thermometer the leads are of stout copper soldered with brass to the platinum leads and separated from each other by mica washers. After the leads have been put in position, a packing of alternate layers of asbestos and mica washers is placed on the slate block, as shown in the figure, and by means of the screw-gland D is forced into all the interstices—the instrument thus being made tight under the pressure. Four leads are used, two being joined by the measuring-wire, the other two being joined directly together*.

### *Description of the Resistance-Measuring Apparatus.*

In order to readily eliminate the changes of resistance of the leads, an equal-arm slide-bridge was employed. The connexions are shown diagrammatically in fig. 2.

In the arm A are placed the main leads; in the opposite arm B are the compensating leads in series with the resistance-box. In the arms C and D are two carefully adjusted equal coils, each having a resistance of about 8 ohms. The bridge-wire is of platinum-iridium, and is half a metre long; its resistance is 0·2980 ohm at 15° C. This wire was calibrated by Carey Foster's method, and, for the degree of accuracy required (0·001 ohm), was found to be of sensibly equal resistance per unit length throughout.

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* For permission to use the compensators (the invention of Mr. Callendar), I am indebted to the Cambridge Scientific Instrument Company.

The galvanometer, a very dead-beat astatic instrument, had a resistance of about 100 ohms. The magnet system and mirror were suspended by a quartz fibre 1·5 inches long, and was damped by a specially large mica damper very closely enclosed.

The scale was placed 4 feet from the mirror, so that a change of resistance of 0·0005 ohm could be readily detected.

The resistance-box was an ordinary plug series box with platinoid coils. It was, in the first instance, calibrated by Mr. E. Wilson, of King's College; but after considerable use so much trouble was given and, indeed, so many experiments spoiled through the inefficiency of the plugs, that links, screwed up by a screwdriver, were substituted for them. Although the links are not so convenient to work with as the plugs, the results have been in every way satisfactory since this change. I then re-calibrated the box, and the two determinations were in fair agreement. Below I give a table of the values of the coils used during the experiments:—

| Nominal value of coil. | Calibrated value at 11° C. | |
|---|---|---|
| ohms. | ohms. | |
| 0·5 | 0·5063 | In terms of my coil, C.L.C. 417. |
| 1 | 1·0042 | |
| 2 | 2·0020 | |
| 2 | 2·004 | |
| 5 | 5·013 | |

As the working stroke in the Otto cycle only occurs once in four strokes of the piston, and as the temperature had to be measured at particular parts of that stroke, it was necessary that the galvanometer should only be in circuit at the right moment, otherwise the galvanometer swing would not give an indication of the true temperature of the wire. During each explosion stroke the measuring-wire goes through the whole cycle of temperature and, in order to secure a particular epoch of this stroke, the following arrangement of contact makers (shown in fig. 3) was designed. The galvanometer circuit was broken in two places, one of which was made during every working stroke, and the other at a definite epoch at every revolution; thus the galvanometer circuit was only completely made at one definite point in every working stroke. At any required point in the stroke of the piston, contact is made every revolution by a cam (C) on the crank-shaft of the engine lifting one end of a vibrating lever, depressing a wire (B), fixed to the other end, into a mercury cup D, and thus making a galvanometer contact for a definite time (about $\frac{1}{20}$ of the stroke) at a certain fraction of the stroke. This, however, makes contact once every revolution, while the temperature is measured only during an explosion stroke. To ensure that the galvanometer circuit shall only be made during every working stroke, it is again broken and only made at the proper time by a relay. This relay is on a separate circuit which is completed by means of a steam-engine indicator (P), whose pencil is replaced by a metal point. During the compression and exhaust strokes the pencil bears on a boxwood cylinder, but when the explosion occurs the arm is forced upwards by the pressure and the pointer makes contact on a strip of brass Q, thus completing the relay circuit. The electromagnet is excited and the beam depressed, completing the galvanometer circuit through the mercury cups R and S. As soon as the relay has moved through a small distance, the indicator break is short-circuited by the mercury cup T, and thus the relay circuit remains closed until broken by a contact on the exhaust-valve of the engine. Although somewhat complicated this relay was found to work well, but great care had to be taken that the contacts were all well amalgamated and the mercury clean, otherwise the very small currents in the galvanometer circuit, when a balance is nearly obtained, are entirely broken by any dirt or grease.

To make a determination of the temperature at any required point the contact-maker on the engine-shaft was set, by means of marks on the driving pulley, to make contact at the required position of the piston. An approximate balance was then found by putting a suitable resistance in the box and adjusting the position of the slider on the wire. If the temperature had been the same at the same point in the stroke in every working stroke, an accurate balance could have been obtained by shifting the slider till the deflexion of the galvanometer was reduced to zero, but this, however, was not the case, and no attempt in the later work was made to obtain an accurate balance on the bridge-wire. The slider was set in such a position that the galvanometer threw about six scale-divisions to one side of zero, and ten successive throws observed. The slider was then moved until the galvanometer threw about six divisions on the other side, and ten throws observed. By taking the mean of these and interpolating, the true reading on the bridge-wire was obtained.

The gas-pressure was rising towards the end of the experiment from 1·6 to 1·9 inches of water.

Below I give a specimen page of my note-book :—

Resistance in box 2·2 ohms.

Bridge-wire.

| Galvanometer-throws at | 500 | 200 | 300 |
|---|---|---|---|
| | 6 left | 3 right | 2 right |
| | 5 | 14 | 0 |
| | 7 | 5 | 10 |
| | 8 | 16 | 3 |
| | 7 | 7 | 7 |
| | 3 | 15 | 12 |
| | 4 | 24 | 5 |
| | 10 | 10 | 16 |
| | 4 | 15 | 17 |
| | 6 | 25 | 3 |
| Mean ......... | 6·0 left | 13·4 right | 7·5 right |

Taking the throws at 500 and 300 we obtain, by interpolation from the throws, a bridge-wire reading of 407, and taking those at 500 and 300 we obtain a reading of 411.

One division on the galvanometer-scale corresponds to from 15 to 50 divisions of the bridge-wire scale, the former figure being for points towards the end of the stroke, and the latter for points towards the commencement of the stroke of the engine. As a check on this method, I have taken the bridge-wire reading from three points or more instead of two, and have found the results obtained agreed within a few scale-divisions of the bridge-wire. To be accurate, this method presupposes constancy in the testing battery, and in the earlier work considerable trouble was found from the variation of the battery, which was two Leclanché cells. In the later work, both in the determination of the fixed points of the thermometers and for the experiments in the gas-engine, a single Daniell cell with an added resistance of about 20 ohms was used, and even after many hours' work was found perfectly constant.

There now remains the question, when the resistance of the measuring-wire at any point has been determined, what temperature on the air-scale corresponds to the resistance found. Callendar has shown that if temperature, in degrees Centigrade, be denoted by $t$, and $pt$ denotes what is called the platinum temperature, then

$$t - pt = \delta\left(\frac{t^2}{100^2} - \frac{t}{100}\right),$$

where $\delta$ is a constant which has to be determined for any particular platinum wire; $pt$ is defined as equal to

$$100\,\frac{R - R_0}{R_1 - R_0},$$

where $R_0$ is the resistance of the wire in melting ice, $R_1$ is the resistance of the wire in steam at atmospheric pressure, and R the resistance of the wire at the temperature $t$*.

As my thermometers consisted of very fine naked wires which were, of necessity, exposed to the erosive action of high-temperature gases, it could not be expected that the fixed points, *i. e.* the resistance in ice and steam, would remain constant after the wire had been in the cylinder for any length of time. Also, owing to the irregular working of the gas- and air-valves, the temperatures reached in the cylinder sometimes far exceeded the mean. When one of these abnormal explosions occurred the wire was sometimes completely fused, and more frequently melted on the surface. These two causes necessitated a frequent determination of the fixed points and also of the value of $\delta$.

Three sizes of measuring-wire were used: they were all about ¾ inch long, their diameters being 0·003, 0·0025, and 0·002 inch respectively. The weights of these wires are approximately 0·00182, 0·0013, and 0·00081 gramme respectively, whence, taking the specific heat of platinum as 0·037, the thermal capacities are 0·0000673, 0·0000481, and 0·00003 gramme-degrees respectively.

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* Phil. Trans. A. 1887.

I had intended to measure the temperatures by means of all three wires, and from the results obtain a curve giving the lag of the wires; this was, however, not possible owing to want of time and apparatus, but the two finer wires gave temperatures which were nearly equal, while the coarser wire gave results somewhat lower than the two others. This induced me to work with the 0·0025 wire for the bulk of the experiments, as the 0·002 wire had so little mechanical strength that, if an abnormal explosion occurred, it was invariably destroyed.

### *Calibration of the Thermometers.*

The ice points call for no special remark beyond the fact that, in spite of considerable care in ensuring a mixture of finely crushed ice and water, they were by no means as satisfactory as the steam points. The average resistance of the 0·003, 0·0025, and 0·002 inch diameter wires was 0·3, 0·55, and 0·75 ohm respectively. The steam points were obtained in a double-jacketed hypsometer of the ordinary form, and were corrected for barometric pressure when necessary. When working with these very fine wires, it is imperative to guard against the heating effect of the battery current, otherwise discrepant and inaccurate results are obtained. I have found that the Daniell cell, mentioned above, with resistance in the external circuit gave no appreciable heating unless the observations were made too rapidly. (This of course only applies to the ice and steam points; when in the engine battery heating is of no importance.)

Two methods were used to obtain the quantity $\delta$. The first method was a comparison of the fine-wire thermometer with a standard Callendar platinum thermometer, both being placed in a tube heated to a high temperature, thus getting a third point on the curve connecting the air and platinum scales.

The standard thermometer consisted of a spiral of platinum wire of a diameter of 0·008 inch wound on a flat plate of mica and enclosed in a porcelain tube 50 centimetres in length, the flat spiral occupying a length of about 7 centimetres from the closed end of the platinum tube. The fixed points of this thermometer were determined many times in ice and steam, and several times in sulphur and aniline vapours. The values were

$$R_0 = 2{\cdot}936 \text{ ohms},$$
$$R_1 = 4{\cdot}080 \text{ ohms},$$
$$\delta = 1{\cdot}52.$$

I have not been able to detect any change in the zero, although this thermometer has been raised to a bright red heat several hundred times during the last two years.

For the comparison of the two thermometers an ordinary gas-furnace, such as is used for combustion work, was first used, but was abandoned owing to unequal and unsteady heating. After some trials I adopted a tube-furnace heated with gas-coke; from end to end of the furnace (about 2 feet in length) was placed a cast-iron tube 2½ inches diameter outside and ½ inch thick. This tube could be rotated in bearings, and thus the temperature could be kept steady round the circumference. Inside the cast-iron tube, and independently supported, was a thick copper tube in which were placed the two thermometers for comparison, the fine wire of the steel-tube thermometer nearly touching the porcelain tube of the standard. Owing to the great mass of the metal, the temperature in the inner tube changed very slowly, and by regulating the draught a temperature of 500° to 600° C. could easily be obtained. Although this was much better than the gas-furnace, as regards an equal temperature circumferentially, still it could not be assumed that the whole length of the coil of the standard thermometer was at the same temperature as the fine wire on the steel-tube thermometer. During any comparison the standard did not show a variation of more than 2° C. Unfortunately the fine wire having such a small thermal capacity as compared with the standard, may not be at quite the same temperature as the standard if there is even the slightest change in the temperature. For these reasons the values of $\delta$ as determined by this method are not so satisfactory as might be wished.

In the second method the resistance of the steel-tube thermometer was determined in sulphur vapour as well as in ice and steam. The sulphur was boiled in an apparatus similar to the first form used by Callendar and Griffiths in their determination of the boiling-point of sulphur *. This consisted of a boiler and condenser made of iron tubes. While this method gives very accurate and satisfactory results, it requires extreme care and takes several hours to obtain a steady temperature.

### *Results of the Experiments.*

It was not until the summer of 1894 that I was able to make any proper experiments with the wires in the cylinder of the gas-engine. I directed my attention at first to the determination of the best speed for the engine, and to find what conditions were necessary to obtain regularity and to ensure that the measuring-wire should follow the temperature of the expanding gases. I found that to obtain regular and perfect combustion of the gases, the water-jacket of the cylinder had to be kept at a temperature of from 50° to 60° C., otherwise abnormal explosions were frequent. The speed of the engine was kept constant at about 120 revolutions per minute, and the wire was found to follow the cycle at this speed except at the beginning of the stroke. The number of explosions per minute was from 12 to 14, each explosion being followed by about 20 blank strokes. The effect of the thorough "washing-out" of the products of combustion from the cylinder and of the hot cylinder jacket was to produce a temperature in the cylinder as high as, if not higher than, if the engine had been working at full load. The small number of working strokes per minute enabled observations to be made with the galvanometer which would not have been possible at much closer intervals of time. The wear and tear on the measuring-wire was reduced, it being a matter of considerable importance to expose the wire to as few explosions as possible.

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* Phil. Trans. A. 1891.

In all the following experiments the thermometer measuring-wire was placed on the axis of the cylinder and in the centre of the compression space.

Two thermometers were used, both practically of identically the same construction as described above. The results of a number of experiments are given below; I have selected those which I have reason to believe are the most complete and accurate of the number which I have made. Wherever I have been able, I have given the constants of the thermometers which were determined before and after the experiments; where it is not given it is because the wire fused before a re-calibration could be made.

*January* 1*st*, 1895.

Thermometer No. 5. Wire 0·003 inch diam.
Air temperature 9° C. Circulating water, 46° C.

$R_0$ before, 0·324 ohm. $R_1 - R_0 = 0{\cdot}1206$. $\delta = 1{\cdot}52$.
$R_0$ after, 0·340 ohm.

| First Set. | | | |
|---|---|---|---|
| Percentage of stroke. | Observed Resistance, ohms. | *pt.* | Temperature on air-scale. |
| 10 | 1·476 | 948 | 1120 |
| 20 | 1·443 | 921 | 1085 |
| 30 | 1·433 | 913 | 1070 |
| 40 | 1·362 | 854 | 990 |
| 50 | 1·351 | 845 | 975 |
| 60 | 1·299 | 802 | 925 |
| 70 | 1·286 | 791 | 900 |
| 80 | 1·238 | 751 | 850 |
| Second Set. | | | |
| 10 | 1·547 | 1007 | 1210 |
| 20 | 1·477 | 949 | 1120 |
| 30 | 1·466 | 940 | 1110 |
| 40 | 1·433 | 921 | 1085 |
| 50 | 1·382 | 871 | 1010 |

It will be noticed that the second set show considerably higher temperatures than the first; this is due to the fact that the former set were taken just before darkness came on, and the second after the gas-pressure had risen considerably. Owing to this I have generally worked in the morning, when the gas-pressure is generally steady except when there is a sudden fog.

*January 2nd*, 1895.

Thermometer No. 4. Wire 0·0025 inch diam.
Circulating water 50° C.

$R_0$ before, 0·5216 ohm. $R_1$ before, 0·7153 ohm. $\delta$ before, 1·397.
$R_0$ after, 0·5357 ohm. $R_1$ after, 0·7328 ohm. $\delta$ after, 2·09.

| Percentage of stroke. | Observed Resistance, ohms. | *pt*. | Temp. on air-scale. $\delta=1·74$. |
|---|---|---|---|
| 10 | 2·474 | 998 | 1245 |
| 20 | 2·455 | 988 | 1230 |
| 30 | 2·366 | 942 | 1150 |
| 40 | 2·306 | 912 | 1120 |
| 50 | 2·248 | 882 | 1060 |
| 60 | 2·128 | 820 | 970 |
| 70 | 2·108 | 810 | 950 |

*January 4th*, 1895.

Thermometer No. 4. Wire 0·0025 inch diam.
Air temperature 10° C. Circulating water 55° C.

$R_0=0·530$. $R_1-R_0=0·1971$. $\delta=1·74$.

| Percentage of stroke. | Observed Resistance, ohms. | *pt*. | Temperature on air-scale. |
|---|---|---|---|
| Explosion | 2·414 | 956 | 1189 |
| 10 | 2·483 | 988 | 1230 |
| 20 | 2·439 | 965 | 1195 |
| 30 | 2·356 | 923 | 1130 |
| 40 | 2·338 | 914 | 1120 |
| 50 | 2·256 | 873 | 1040 |
| 60 | 2·184 | 836 | 990 |
| 70 | 2·094 | 790 | 920 |
| 80 | 1·960 | 722 | 830 |

Thermometer No. 5. Wire 0·003 inch diam.

$R_0$=0·332. $R_1-R_0$=0·1206. $\delta$=1·52.

| Percentage of stroke. | Observed Resistance, ohms. | *pt.* | Temperature on air-scale. |
|---|---|---|---|
| Explosion | 1·444 | 919 | 1080 |
| 10 | 1·476 | 949 | 1120 |
| 20 | 1·451 | 928 | 1095 |
| 30 | 1·439 | 918 | 1080 |
| 40 | 1·395 | 818 | 1025 |
| 50 | 1·392 | 879 | 1020 |
| 60 | 1·333 | 830 | 955 |
| 70 | 1·268 | 776 | 880 |
| 80 | 1·238 | 751 | 855 |

No further experiments were made with this wire as is clearly did not attain the proper temperature.

*January* 31*st*, 1895.

Thermometer No. 4. Wire 0·0025 inch diam.

Air temperature 7·5° C. Circulating water 57° C.

$R_0$ before, 0·562 ohm. $R_1-R_0$ before, 0·220 ohm. $\delta$ before, 1·90.
$R_0$ after, 0·581 ohm. $R_1-R_0$ after, 0·227 ohm. $\delta$ after, 1·90.

| Percentage of stroke. | Observed Resistance, ohms. | *pt.* | Temperature on air-scale. |
|---|---|---|---|
| 10 | 2·562 | 893 | 1100 |
| 20 | 2·595 | 907 | 1125 |
| 30 | 2·524 | 876 | 1080 |
| 40 | 2·445 | 840 | 1020 |
| 50 | 2·360 | 802 | 960 |
| 60 | 2·338 | 792 | 940 |
| 70 | 2·186 | 729 | 850 |
| 80 | 2·151 | 711 | 825 |

*February* 12*th*, 1895.

Thermometer No. 5. Wire 0·002 inch diam.

Air temperature 7° C. Circulating water 43° C.

$R_0$ before, 0·796 ohm. $R_1-R_0$=0·283 ohm.

| Percentage of stroke. | Observed Resistance, ohms. | *pt.* | Temp. on air-scale. $\delta$=1·22. |
|---|---|---|---|
| 10 | 3·662 | 1012 | 1160 |
| 20 | 3·616 | 996 | 1140 |
| 30 | 3·477 | 947 | 1075 |
| 40 | 3·352 | 907 | 1020 |
| 50 | 3·253 | 868 | 970 |
| 60 | 3·120 | 821 | 910 |
| 80 | 3·071 | 804 | 890 |

This wire was destroyed by accident during my absence before a new value of $\delta$ could be determined.

Thermometer No. 4. Wire 0·0025 inch diam.

$R_0=0·592$. $R_1-R_0=0·223$. $\delta=1·90$.

| Percentage of stroke. | Observed Resistance, ohms. | *pt*. | Temperature on air-scale. |
|---|---|---|---|
| Explosion | 2·529 | 878 | 1080 |
| 10 | 2·580 | 891 | 1100 |
| 20 | 2·576 | 890 | 1100 |
| 30 | 2·499 | 855 | 1040 |
| 40 | 2·459 | 837 | 1010 |

The wire partly fused during the observation at 50 per cent. These experiments were made during a period of intense cold, and the indicator diagrams showed the pressures to be lower than usual. The temperatures were lower than those of Jan. 1–5 or March 7–20, otherwise the fine wire on thermometer No. 5 would not have remained intact so long.

### *March 7th.*

Thermometer No. 4. Wire 0·0025 inch diam.

Air temperature 10° C. Circulating water 46° C.

$R_0$ before, 0·537 ohm. $R_1-R_0$ before, 0·208. $\delta$ before, 1·81.
$R_0$ after, 0·551 „ $R_1-R_0$ after, 0·208. $\delta$ after, 1·75.

| Percentage of stroke. | Observed Resistance, ohms. | *pt*. | Temp. on air-scale. $\delta=1·78$. |
|---|---|---|---|
| 10 | 2·437 | 913 | 1115 |
| 20 | 2·450 | 920 | 1120 |
| 30 | 2·381 | 886 | 1090 |
| 40 | 2·333 | 861 | 1060 |
| 50 | 2·304 | 849 | 1015 |
| 70 | 2·204 | 801 | 940 |
| 80 | 2·113 | 757 | 880 |

### *March* 16*th*.

Thermometer No. 4. Wire 0·0025 inch diam.
Air temperature 13° C. Circulating water 50° C.

$R_0$ before, 0·551 ohm. $R_1 - R_0 = 0·207$.
$R_0$ after, 0·551 ohm. $\delta$ (determined by sulphur vapour) 1·75.

| Percentage of stroke. | Observed Resistance, ohms. | *pt*. | Temperature on air-scale. |
|---|---|---|---|
| 10 | 2·434 | 909 | 1100 |
| 20 | 2·354 | 870 | 1045 |
| 30 | 2·364 | 875 | 1050 |
| 40 | 2·236 | 833 | 990 |
| 60 | 2·163 | 778 | 910 |
| 70 | 2·057 | 727 | 840 |

I was so doubtful of the second and third points that I repeated the first three with the results below :—

| | | | |
|---|---|---|---|
| 10 | 2·452 | 917 | 1115 |
| 20 | 2·373 | 879 | 1055 |
| 30 | 2·369 | 877 | 1050 |

### *March* 20*th*.

Same thermometer and wire.
Air temperature 13° C. Circulating water 51° C.

| Percentage of stroke. | Observed Resistance, ohms. | *pt*. | Temperature on air-scale. |
|---|---|---|---|
| 10 | 2·481 | 931 | 1140 |
| 20 | 2·403 | 894 | 1080 |
| 30 | 2·403 | 894 | 1080 |

The temperature was variable throughout this experiment and the wire fused during the observation at 40 per cent.

I consider these experiments to be the most accurate of the whole series.

Towards the end of February I determined to find $\delta$ by means of an observation in sulphur vapour; and as some question had arisen as to the action of the high-temperature gases on the platinum wires, more especially as to the variation of the quantity $\delta$, I gold-soldered a platinum wire 0·002 diameter on No. 5 thermometer, and determined its fixed

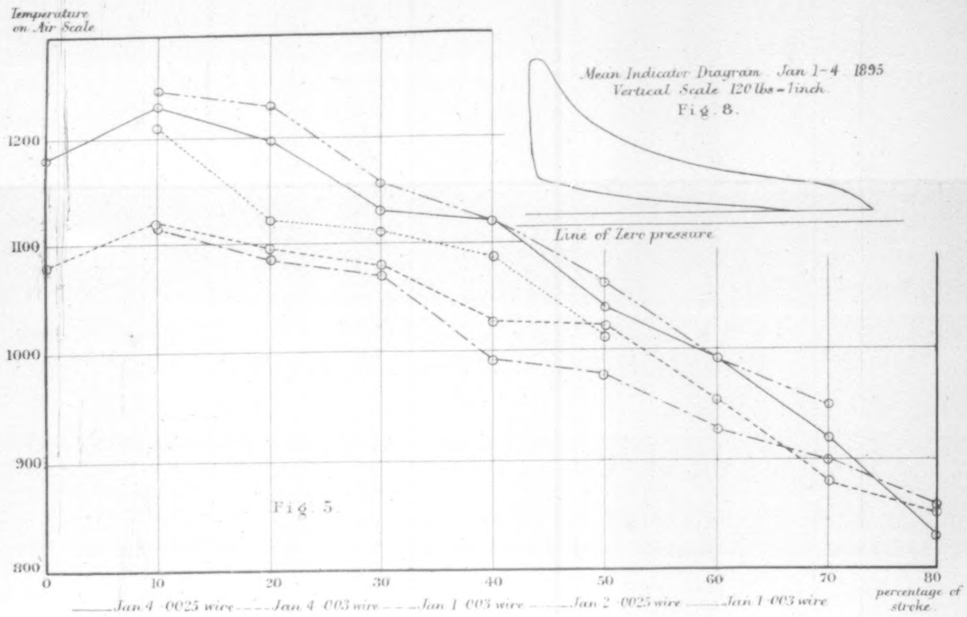

Fig. 5.

Mean Indicator Diagram Jan 1–4 1895
Vertical Scale 120 lbs = 1 inch.
Fig. 8.

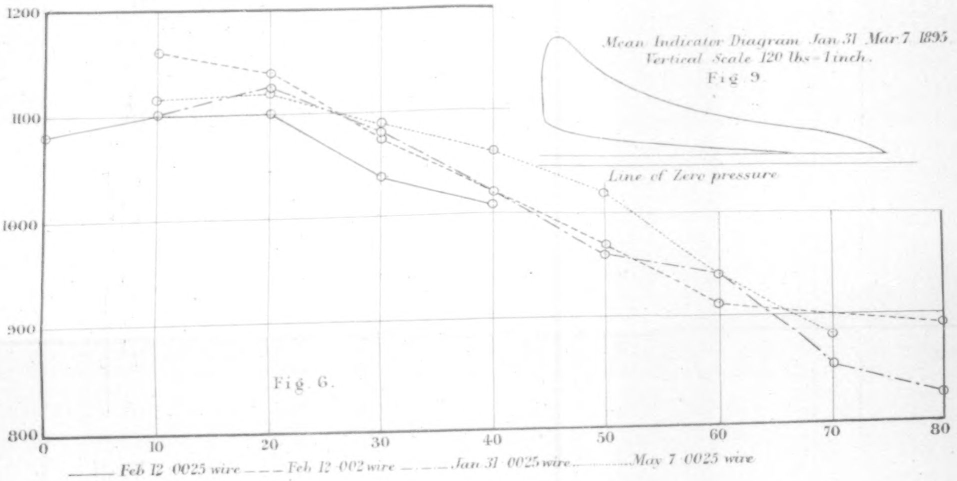

Fig. 6.

Mean Indicator Diagram Jan 31 Mar 7 1895
Vertical Scale 120 lbs = 1 inch.
Fig. 9.

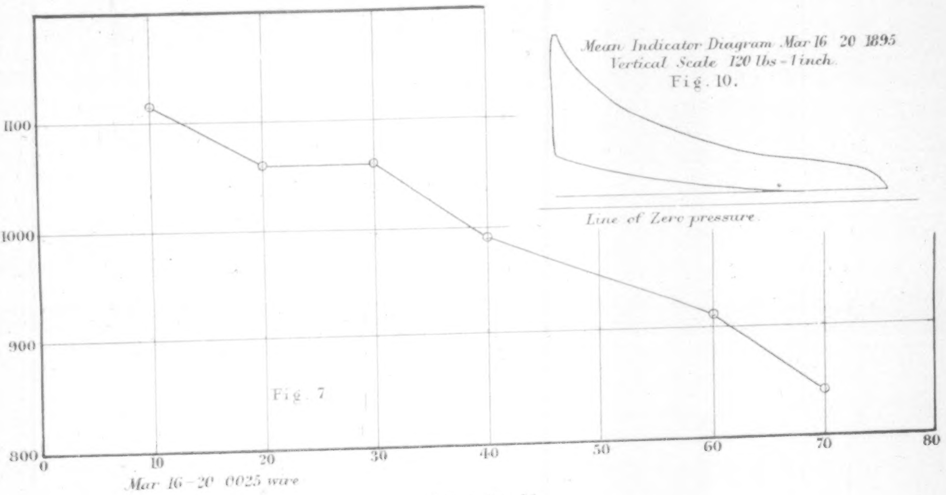

Fig. 7

Mean Indicator Diagram Mar 16 20 1895
Vertical Scale 120 lbs = 1 inch.
Fig. 10.

Mintern Bros. lith.

points and calculated the $\delta$ before this wire was placed in the engine. In every other case the wires had been exposed to the action of the cylinder gases for about half an hour before the determination of the fixed points. In this case the wire had only been exposed to the flame of the blowpipe used in the soldering. The fixed points were $R_0=0{\cdot}7596$; $R_1=1{\cdot}0536$; $\frac{R_1}{R_0}=1{\cdot}32$; $R_1-R_0=0{\cdot}294$; $\delta=2{\cdot}93$.

This value of $\delta$ seemed so high that I repeated the whole of the points without detecting any error in the previous work. The low value of $\frac{R_1}{R_0}$ together with the high $\delta$ seems to indicate that a gold-platinum alloy formed at the junction of the main lead to the fine wire and on the surface of the latter. The thermometer was then placed in the engine on March 16th and gave the following results :—

| Percentage of stroke. | Observed Resistance, ohms. | *pt*. | Temperature on the air-scale. |
|---|---|---|---|
| 10 | 3·527 | 948 | 1200 |

After running in the engine some time the fixed points were re-determined with the results given below :—

$$R_0=0{\cdot}786. \quad R_1=1{\cdot}075. \quad R_1-R_0=0{\cdot}289.$$

$$\frac{R_1}{R_0}=1{\cdot}37. \quad \delta=1{\cdot}95.$$

From this it will be seen that the action of the gases on the cylinder had been such as to bring the wire into a normal condition, most probably by sweeping off any alloy which had been formed.

I have plotted the results of the experiments, and the curves are given in Plate XI. figs. 5, 6, & 7, the corresponding pressure-volume curves being given in figs. 8, 9, & 10. In figs. 5, 6, & 7 the horizontal ordinates show the percentage of the stroke, and the vertical ordinates the temperature in degrees C. on the air-scale, the observed points being marked by small circles. I have divided the experiments up into three groups—the first being from Jan. 1 to Jan. 4, the second from Jan. 31 to March 7, and the last from March 16 to March 20. It will be noticed that those of Jan. 1–4 (fig. 5) show a distinct break in the regularity of the curve, the line falling but little between the 3rd and 4th points on the 0·0025 wire and between the 4th and 5th points on the 0·003 wire, instead of falling regularly throughout as would have been expected. The curves of the second group of experiments (fig. 6) show no trace of irregularity; while those of the third group (fig. 7) show a strongly marked variation between the 2nd and 3rd points. Several explanations of this singularity have suggested themselves to me, but I do not consider them to come within the scope of this paper. I hope to make further experiments bearing on this matter, and to obtain more data on the subject. The results of the experiments of Jan. 31 to March 7 are chiefly interesting as showing the close concordance of temperatures registered by wires of such different thermal capacity, especially when it is remembered that the source of heat used was a very variable one, the pressures, as shown on the indicator cards, varying from day to day, and also during the day, owing to the varying gas-pressure and quality.

I would also point out that a difference of 100 degrees shown on the thermometers corresponds to a distance of about $\frac{1}{12}$ inch on the indicator cards.

In conclusion I must express my thanks to Messrs. Johnson and Matthey for the trouble they have taken in drawing down the wires, several of which were of special diameters. I should have been quite unable to carry out costly experiments of this kind had it not been for the liberality of my brother, Mr. H. R. J. Burstall, who has provided me with the necessary funds. The apparatus has been designed and carried out in conjunction with him; and I wish to express my sincere indebtedness to him for his many suggestions, which have made these experiments possible.

## DISCUSSION.

Prof. PERRY said that an instrument for quickly recording varying temperatures was greatly required by engineers. The temperature just inside the cylinder-walls was, however, most important to determine; and a knowledge of how the temperature from 1 to 2 mm. inside the walls varied would be of the greatest value. He would like to ask the author if the observed temperatures agreed with the values calculated on the assumption that the gases in the cylinder behaved as a perfect gas, and that

$$\frac{PV}{T} = \text{constant}$$

during the whole stroke. Differences between the observed and calculated values might be due to dissociation, and not entirely to lag in the thermometers. It was astonishing that even the fine wires employed were able to follow the rapidly varying temperature, and he would like to see some special experiments made to test this point.

Prof. CAPPER showed a diagram giving the values calculated on the assumption that

$$\frac{PV}{T} = \text{constant}.$$

In such a calculation it was necessary to assume some temperature as a starting point, and in general this temperature was obtained from an analysis of the exhaust gases, so that the calculated curve is most likely to depart from the truth at the commencement of the stroke. He (Prof. Capper) hoped that the author would be able to accurately determine the temperature of some one point of the stroke, and he suggested that the point where the observed curve crossed the theoretical curve would be the most suitable one for this purpose. Such a point must exist, since at the commencement of the stroke the lag causes the observed temperature to be too low, while at the end of the stroke the observed temperatures are too high. Mr. Burstall finds a curious bump in his curves, and it is curious that a similar bump exists in the calculated curves. From the constancy with which this bump appears, it would seem that it must have some physical meaning. It was important to remember that the expansion of the gas-engine cylinder is not adiabatic, for heat is both abstracted and generated during the stroke.

Mr. BLAKESLEY suggested that since the temperatures dealt with were sufficient to make the wire red-hot, the question of lag might be investigated by means of Becquerel's phosphoroscope at a known interval after the removal of the source of heat.

Mr. GRIFFITHS said he considered an important source of error was the large thermal capacity of the leads when the working wire was so very short. He thought it would be possible to standardise the thermometers under conditions somewhat similar to those which occur in the engine cylinder. Thus, perhaps alternate gushes of air at 0° and 100° C. might be used. The use of gold to attach the fine wire to the leads was objectionable, since the gold must permeate the platinum for quite an appreciable fraction of the whole length of the wire. He would like to know whether the change in $\delta$ alluded to by the author occurred with the first explosion or whether it was a gradual one.

Mr. Enright pointed out that the nature of the working substance in a gas-engine varied during the stroke.

Prof. Perry said that the change in the specific volume of the gases before and after combustion did not amount to more than 1·25 per cent.

Mr. E. Wilson said he thought it was most important to shorten the time of contact, since at present the galvanometer readings corresponded to the mean temperature over a range of about 5 per cent. of the whole stroke. It might be possible to make use of a condenser to get over this difficulty.

Prof. Rücker said that the Kew Observatory were making arrangements to undertake the testing of platinum thermometers.

Mr. Enright suggested that with a very short contact induced currents might cause errors.

Mr. Rhodes said he had found that the method of determining the zero-point of thermometers by means of melting ice was far from satisfactory, and that the results obtained could not be depended upon to within 0°·1 C.

The Author, in his reply, said the only chemical action on the wires he thought probable was the formation of a carbide. After several hours' use, however, the wires appear quite bright and clean.

## L. *A New Method in Harmonic Analysis.*

### *By* ARCHIBALD SHARP.*

[Abstract.]

THE author, in this paper, applies the principle of the form of harmonic analyser for giving direct readings of the amplitude and epoch of the various constituent harmonic terms previously described by him, to the performance of harmonic analysis without the use of an instrument. The kinematic principle is as follows:—Let the curve to be analysed be drawn, with a scale of abscissæ such that the period is $2\pi$. Let a wheel, $w$, roll on the paper and be connected with a tracing-point, P, in such a manner that as P moves uniformly in the $x$ direction the axis of the wheel $w$ turns uniformly counter-clockwise in a horizontal plane, and the distance rolled through during any short interval is equal to the corresponding displacement in the tracer P in the $y$ direction. The curve traced out by $w$ the author calls the roller curve, and from the vector joining the initial and final points of this curve the amplitude and epoch can be determined. Suppose the periodic curve consists of a portion of the curve,

$$y = a_0 + a_1 x + a_2 x^2 + a_m x^m,$$

repeated over and over again; then if the tracer is taken round this periodic curve you get a rolled curve, which may be called the first rolled curve. If now the curve whose ordinates are

$$\frac{dy}{dx}$$

is traced out, the roller curve obtained is the evolute of the first, and so on for

$$\frac{d^2y}{dx^2}, \text{ \&c.}$$

The author gives two worked examples, and compares the values of the coefficients obtained with those given by the harmonic analyser of the Guilds Central Technical College.

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* Read May 10, 1895.

## LI. *The Thermal Constants of the Elements.*

*By* N. F. Deerr.*

[Abstract.]

The author has found that there is considerable evidence in favour of the following relations existing between one metal and another, or between one non-metal and another, in any group of elements in the periodic classification.

1. $(T+L/S)C = \text{const.}$ 2. $T.C = \text{const.}$ 3. $L.C/S = \text{const.}$; where T denotes the absolute temperature of fusion; L the latent heat of fusion, per unit mass; S the mean specific heat between the absolute zero and the melting point; C the mean coefficient of expansion between the same units.

On the opposite page is a chart of the periodic classification of the elements with values of the quantities mentioned above, so far as they can be calculated with the present available data; in the absence of other data the values of S and C have been taken between 0° C. and 100° C.

It will be seen on reference to the annexed table that whereas in the majority of cases the agreement is most striking, the only entirely discordant element is mercury. In the eighth group the three or four elements in one horizontal line agree, this being particularly marked in the values of T.C; these values, however, decrease slightly in passing down from one series to another.

The author obtained the first relation by assuming the total heat of liquefaction of unit mass and the heat required to expand unit mass of that body through any fraction of its initial length to be directly proportional to intermolecular attraction: the second and third relations were obtained by combining the first relation with one recently brought forward before the Chemical Society by Mr. Holland Crompton (Trans. cxlv. p. 240):—$A . L/T = \text{Valency} \times \text{Const.}$, where A denotes the atomic weight; in this way the first relation may be considered as composed of the second and third.

All the data used are to be found in Landolt and Börnstein's Tables and in Dammer's 'Inorganic Chemistry,' with the exception of these latent heats:—Sodium and Potassium, Joannis; Gold, Rose; Aluminium, Richards; Thallium, Neville and Heycock.

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* Read June 14, 1895.

| | I. | II. | III. | IV. | V. | VI. | VII. | VIII. | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Li.** | **Be.** | **B.** | **C.** | **N.** | **O.** | **F.** | | | | |
| | Na. | Mg. | Al. | Si. | P. | S. | Cl. | | | | |
| (T+L/S)C... | ·0337 | ... | ·0231 | ... | ·042 | ·0278 | ... | | | | |
| T.C ......... | ·0260 | ·0207 | ·0201 | ·0112 | ·039 | ·0246 | ... | | | | |
| L.C/S ...... | ·0077 | ... | ·003 | ... | ·003 | ·0032 | ... | | | | |
| | K. | Ca. | Sc. | Ti. | V. | Cr. | Mn. | Fe. | Co. | Ni. | ... |
| (T+L/S)C... | ·0359 | ... | ... | ... | ... | ... | ... | ·0254 | ... | ... | ... |
| T.C ......... | ·0280 | ... | ... | ... | ... | ... | ... | ·0228 | ·022 | ·021 | ... |
| L.C/S ...... | ·0079 | ... | ... | ... | ... | ... | ... | ·0026 | ... | ... | ... |
| | Cu. | Zn. | Ga. | Ge. | As. | Se. | Br. | | | | |
| (T+L/S)C... | ... | ·0278 | ... | ... | ... | ... | ·146 | | | | |
| T.C ......... | ·0248 | ·0192 | ... | ... | ·0038 | ·0217 | ·093 | | | | |
| L.C/S ...... | ... | ·0086 | ... | ... | ... | ... | ·053 | | | | |
| | Rb. | Sr. | Yt. | Zr. | Nb. | Mo. | ... | Ru. | Rh. | Pd. | ... |
| (T+L/S)C... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ·0263 | ... |
| T.C ......... | ... | ... | ... | ... | ... | ... | ... | ·0199 | ·0193 | ·0191 | ... |
| L.C/S ...... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ·0072 | ... |
| | Ag. | Cd. | In. | Sn. | Sb. | Te. | I. | | | | |
| (T+L/S)C.. | .0319 | ·0276 | ... | ·0210 | ... | ... | ·142 | | | | |
| T.C ......... | ·0244 | ·0194 | ·0193 | ·0141 | ·0081 | ·0127 | ·091 | | | | |
| L.C/S ...... | ·0075 | ·0082 | ... | ·0070 | ... | ... | ·051 | | | | |
| | Cs. | Ba. | Di. | Ce. | ... | ... | ... | | | | |
| | ... | ... | ... | ... | ... | ... | ... | | | | |
| | ... | ... | Er. | La. | Ta. | W. | ... | Os. | Ir. | Pt. | Au. |
| (T+L/S)C... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ·0256 | ·0263 |
| T.C ........ | ... | ... | ... | ... | ... | ... | ... | ·0182 | ·0173 | ·0180 | ·0190 |
| L.C/S ...... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ·0076 | ·0073 |
| | ... | Hg. | Tl. | Pb. | Bi. | ... | ... | | | | |
| (T+L/S)C... | ... | ·0191 | 0225 | ·0210 | ·0129 | ... | ... | | | | |
| T.C ......... | ... | ·014 | ·0173 | ·0163 | ·0071 | ... | ... | | | | |
| L.C/S ...... | ... | ·0051 | ·0052 | ·0047 | ·0058 | ... | ... | | | | |

## LII. *The Thermal Properties of Isopentane.*

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### INTRODUCTION.

THE relations between the temperatures, pressures, and volumes of gases and liquids have been the subject of numerous experimental and mathematical investigations since the publication of the classical experimental researches of Andrews, and the great mathematical investigation of van der Waals on the continuity of the gaseous and liquid states of matter. Among the substances which have been most thoroughly studied are the elementary gases—oxygen, nitrogen, hydrogen; a few compounds which are gaseous under ordinary conditions, such as carbon dioxide and ethylene; and a few liquids, especially ether, the lower alcohols, and water.

The experiments on oxygen, hydrogen, and nitrogen have necessarily been chiefly carried out at temperatures far above their critical points, whilst with ethylene and carbon dioxide the range of temperature below the critical temperature at which observations have been made is small. It is also, as a rule, more difficult to fill a tube with a gas in a perfectly pure state than with a liquid.

Of the liquids examined, the alcohols and water behave abnormally in many respects, owing probably to the existence of complex molecules in the liquid state; and though the results obtained are of great interest, it is obvious that a thorough investigation of what may be termed normal substances should be carried out before the behaviour of such abnormal compounds can be properly understood.

None of the substances yet examined have given better results than ethyl ether. It can be obtained without great difficulty in a state of purity; it is possible to obtain results through a considerable range of temperature both above and below its critical temperature, and its critical pressure is moderately low.

Experiments on ether over a wide range of volume and temperature have been made by Ramsay and Young (Phil. Trans. 1887, A, p. 57), and also by Battelli (*Mem. della R. Ac. di Torino*, [2] xl. 1889), and up to extremely high pressures—though with a small range of volume—by Amagat (*Annales Chim. Phys.*, series 6, vol. xxix.), and by Barus (Phil. Mag. 1890, vol. xxx. p. 358).

The result of these investigations is to show that although the formula of van der Waals, $\left(p+\frac{a}{v^2}\right)(v-b)=\mathrm{RT}$, gives the general form of the isothermal curves very satisfactorily and, indeed, agrees well with the experimental results at large volumes, yet it cannot be regarded as sufficiently accurate at volumes near and below the critical volume.

At constant volume, however, since $\frac{a}{v^2}$ and $(v-b)$ are both constants, the formula of van der Waals may be reduced to the form $p=b\mathrm{T}-a$, where $a$ and $b$ are constants depending on the nature of the substance and on the volume*.

This relation was found to hold good by Amagat (*Comptes Rendus* (1882), xciv. p. 847) in the case of carbon dioxide and ethylene in the gaseous state and approximately in the liquid state, and by Ramsay and Young (Phil. Mag. May 1887, p. 435) in the case of ether in both the gaseous and liquid states.

Barus (*loc. cit.*) has shown that the law holds good for ether and some other substances in the liquid state up to a pressure of 1000 atm., but that there are deviations at higher pressures. Up to 1000 atm. he estimates the error as not greater than 2 or 3 degrees.

Further investigations by Ramsay and Young (Phil. Mag. August 1887, p. 195) have shown that the law is applicable, approximately at any rate, to methyl and ethyl and (Phil. Trans. 1889, A, p. 137) propyl alcohol, but that there are considerable deviations in the case of water (Phil. Trans. 1892, A, p. 107).

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* The symbols $b$ and $a$ in the equation $p=b\mathrm{T}-a$ have, of course, not the same meaning as in van der Waals's equation, but as they have been used in previous papers by Ramsay and myself I have thought it best to adhere to them.

Further experiments—up to very high pressures, though with a small range of volume—have been carried out by Amagat (*Ann. Chim. Phys.* loc. cit.), and his conclusions will be referred to later.

The number of substances that can be conveniently investigated through a sufficiently wide range of temperature both above and below the critical temperature and through a wide range of volume (in both the gaseous and liquid states) is very limited; it therefore seemed desirable to take advantage of the opportunity, afforded by the possession of a quantity of pure isopentane, to make as complete an investigation as possible of the relations between the temperature, pressure, and volume of this substance. It would be difficult to find a more suitable liquid; it is extremely stable and is readily freed from moisture by distillation over phosphorus pentoxide; its boiling-point is 27°·95; its critical temperature is 187°·8, and its critical pressure 25020 millim.

## Experimental Results.

### *Preparation of Pure Isopentane.*

A quantity of "pentane" was procured from C. A. F. Kahlbaum of Berlin, who has kindly informed me that the substance is obtained as a bye-product in the preparation of amylene from amyl alcohol, the admixed amylene being separated by means of bromine. The isopentane was shaken with concentrated sulphuric acid and afterwards repeatedly with a mixture of concentrated sulphuric and nitric acids. The action in each case was at first somewhat violent, but it moderated after several additions of the acids had been made.

After standing all night over sulphuric and nitric acids the isopentane was again repeatedly shaken with sulphuric acid—which was at first coloured a deep orange; it was then treated with a strong solution of potassium hydrate, washed with water, dried with solid potassium hydrate, and distilled*.

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* It is possible that the substance might have been satisfactorily purified by treatment with bromine. The loss by evaporation would probably have been smaller and the process less troublesome.

The greater portion came over below 32°, but the temperature finally rose to 56°.

The isopentane, which in addition to the higher-boiling impurity contained a small quantity of a very volatile substance, was then fractionated ten times, and was finally collected in two fractions both of which boiled quite constantly at 27°·45 under a pressure of 748·5 millim.

### *Proofs of Purity of the Isopentane.*

It seemed at first rather doubtful—from its method of formation and from its behaviour with sulphuric and nitric acids—whether the isopentane could be obtained in a pure state; but the impurities were removed without much difficulty by fractional distillation, and the following evidence leaves no doubt that the substance was satisfactorily purified:—

1. The two fractions boiled at precisely the same temperature and both quite constantly.
2. The specific gravities of the two fractions at 0° were practically identical (0·63925 and 0·63922).
3. The critical temperatures and pressures of the two fractions were in very close agreement (see p. 609).
4. The vapour-pressures of both fractions were determined at a great number of different temperatures and agreed very well together.
5. The vapour-pressure was found to be entirely independent of the relative volumes of liquid and vapour. The experimental results at two temperatures, 90° and 140°, have already been published in a paper read before the Physical Society (Phil. Mag. Dec. 1894, p. 569; *ante*, p. 271). The object of the paper was to show that the vapour-pressure *of a pure substance* at any temperature is independent of the relative volume of liquid and vapour; but since it is well known that the vapour-pressure of an impure liquid does depend on the volume*, the invariability of the vapour-pressure in the

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* It is true that in a limited number of special cases a particular mixture of two substances at a given temperature exerts a lower vapour-pressure than any other mixture (*e. g.* formic acid and water), or a higher vapour-pressure (*e. g.* propyl alcohol and water), and that the vapour-pressure of such a mixture at that temperature is independent of the relative volumes of liquid and vapour; also that such a mixture

case of my specimen of isopentane may perhaps be adduced as evidence in favour both of the purity of this particular substance and of the behaviour of pure substances in general. In any case the other proofs of purity appear to be sufficient.

6. In the course of the determinations of the volume of a gram of vapour with a modified Hofmann's vapour-density apparatus the vapour-pressure was measured at a few temperatures, and a comparison of these pressures with those read from the curves constructed from the data obtained by the dynamical method shows that the agreement is satisfactory.

Vapour-Pressure.

| Temperature. | Statical. | Dynamical. | Δp. | Δt. |
|---|---|---|---|---|
| 10°·6 | 401·0 | 400·0 | +1·0 | −0·05 |
| 10·85 | 405·6 | 403·95 | +1·65 | −0·1 |
| 11·05 | 406·1 | 407·15 | −1·05 | +0·05 |
| 16·55 | 499·6 | 503·6 | −4·0 | +0·2 |

7. The agreement of the boiling-point, specific gravity, vapour-pressures at high temperatures, and critical constants with those of a specimen of isopentane prepared by G. L. Thomas and myself from amyl iodide.

### *Boiling-Point.*

The isopentane was always distilled over phosphorus pentoxide immediately before being used for any determination, and there are thus a considerable number of observations of the boiling-point. They are given in the table below, together with the boiling-points corrected to 760 millim. pressure.

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would boil at a constant temperature and distil unchanged in composition under that pressure; but it has been found in such cases that the composition of the mixture which has a maximum or minimum vapour-pressure (and a constant boiling-point) differs to some extent at different temperatures (and pressures). In such a case, therefore, it might be found at a certain temperature that the vapour-pressure of the mixture was independent of the relative volumes of liquid and vapour, but it is in the highest degree improbable that a similar result would be obtained with the same mixture at a widely different temperature.

The value of $dp/dt$ at the boiling-point = 26·2 millim. The boiling-point, calculated from the constants for Biot's formula, is 27°·95.

| Fraction A. | | | Fraction B. | | |
|---|---|---|---|---|---|
| Pressure. | Temperature. | | Pressure. | Temperature. | |
| | Observed. | Corrected to 760 mm. | | Observed. | Corrected to 760 mm. |
| 745·4 | 27°·3 | 27·85 | 748·5 | 27·45 | 27·9 |
| 748·5 | 27·45 | 27·9 | 751·1 | 27·55 | 27·9 |
| 749·0 | 27·55 * | 27·95 | 751·2 | 27·6 | 27·95 |
| 751·2 | 27·6 | 27·95 | 751·5 | 27·65 * | 27·95 |
| 753·5 | 27·7 | 27·95 | 752·4 | 27·65 * | 27·95 |
| 758·9 | 27·9 * | 27·95 | 759·1 | 27·95 * | 28·0 |
| 759·1 | 27·95 * | 28·0 | 761·7 | 28·0 | 27·95 |
| 761·9 | 28·0 | 27·95 | | | |
| 765·3 | 28·15 | 27·95 | | Mean ...... | 27·95 |
| | Mean ...... | 27·95 | | | |

* The temperatures marked with an asterisk were determined with a Geissler's normal thermometer.

*Boiling-Points by other Observers.*

| Name. | Reference. | Pressure. | B.P. | B.P. reduced to 760 millim. |
|---|---|---|---|---|
| 1. Schmidt ........ | *Annalen*, cclxvi. p. 282. | 760·7 | 31°–33° | 31°–33° |
| 2. Pawlewski ...... | *Ber.* xvi. p. 2633. | 760 | .. | 31 |
| 3. Schiff .......... | *Annalen*, ccxx. p. 87. | 760 | .. | 30·5–31·5 |
| 4. Perkin .......... | Trans. Chem. Soc. xlv. p. 445. | 760 | .. | 29–32 |
| 5. Thorpe and Rodger | Phil. Trans. clxxxv. A, p. 453. | 760 | .. | 30·4 |
| 6. Schorlemmer .... | Proc. Roy. Soc. xvi. | 760 | .. | 30 |
| 7. Goldstein ........ | J. Russ. Chem. Soc. 1882, p. 45. | 760 | .. | 30·5 |
| 8. Beilstein and Kurbatow .. | *Ber.* xiv. p. 1620. | .. | .. | 30 |
| 9. Wurtz .......... | *Annalen*, cxxviii. p. 229. | .. | .. | 28–30 |
| 10. Pelouse and Cahours .. | *Jahresb.* xvi. p. 527. | .. | .. | 30 |
| 11. Lachowitz ...... | *Annalen*, ccxx. p. 188. | .. | .. | 29–30 |
| 12. Frankland ..... | Trans. Chem. Soc. iii. pp. 31 & 481. | 734 | 30 | 31 |
| 13. Just .. ......... | *Annalen*, ccxx. p. 146. | .. | .. | 30 |
| 14. Landolt and Jahn . | *Zeit. Phys. Chem.* x. p. 290. | 760 | .. | 28 |
| 15. Altschul ........ | *Ibid.* xi. p. 590. | 760 | .. | 28 |

Mr. J. W. Rodger has kindly informed me that he has prepared specimens of isopentane from amyl iodide obtained from both Scotch and

Irish samples of amyl alcohol, and that they boiled within 0°·05 and 0°·02 respectively. The observed boiling-points were:—

From Irish amyl alcohol.... 28°·04,
„ Scotch „ „ 28°·01.

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1. Obtained from Trommsdorff (from American petroleum) dried with phosphorus pentoxide and fractionated. Schmidt states that the sample contained a considerable quantity of normal pentane.
2. Source not stated.
3. Separated from commercial amylene by treatment with sulphuric acid diluted with its own weight of water. Residue treated with concentrated sulphuric acid until the acid was no longer coloured. Distilled and heated to 130° with sodium.

4–6. Specimens prepared by Schorlemmer from petroleum.
8. From Caucasian petroleum.
9. From crude amylene by action of bromine.
10. From American petroleum.
11. From petroleum from Galicia.
12. By action of zinc and water on amyl iodide.
13. By action of zinc and hydrochloric acid on amyl iodide.

14, 15. Separated from amylene by means of bromine. The substance is called "pentane."

As these observations of the boiling-point of isopentane, with the exception of those of Landolt and Jahn, Altschul, and Rodger, are considerably higher than mine, a specimen of isopentane was prepared by Thomas and myself from amyl iodide; the method of preparation and the observations of the boiling-point, specific gravity, and critical temperature and pressure are given in a separate paper. These observations agreed perfectly with those described in this paper. The boiling-point was 27°·95 at 760 millim.

### *Specific Gravity.*

The specific gravity of each fraction was determined at two different temperatures by Sprengel's method as modified by Perkin. The weighings were reduced to a vacuum.

| Temperature. | Fraction A. | Fraction B. |
|---|---|---|
| 0° | 0·63925 | 0 63922 |
| 14°·4 | 0·62514 | |
| 13°·45 | ... | 0·62614 |

The specific gravity at 0° of the sample prepared by Thomas and myself was ·63935.

*Specific Gravities by other Observers.*

| Name. | Sp. gr. at $t°$. | | Sp. gr. at 0°. |
|---|---|---|---|
| Schiff | 0·6282 | at 13°·7 | 0·6416 |
| Pelouse and Cahours | 0·628 | ,, 18 | 0·6458 |
| Frankland | 0·6413 | ,, 11·2 | 0·6524 |
| ,, | 0·6385 | ,, 14·2 | 0·6526 |
| Just | 0·6375 | ,, 13/13 | 0·6500 |
| Bartoli and Stracciati * | 0·6402 | ,, 0 | 0·6402 |
| Landolt and Jahn | 0·62656 | ,, 14·3 | Mean ... 0·64058† |
| ,, ,, | 0·62472 | ,, 16·2 | |
| ,, ,, | 0·62278 | ,, 18·2 | |
| ,, ,, | 0·62074 | ,, 20·0 | |
| Perkin | 0·62479 | ,, 15/15 | 0·63893 |
| ,, | 0·61590 | ,, 25/25 | 0·63888 |

The specific gravities at 0° were calculated from the observations at higher temperatures by means of the formula

$$D_t = 0{\cdot}63923 - 0{\cdot}0_3958\,t - 0{\cdot}0_513\,t^2.$$

This formula agrees very well with my experimental results up to 60°.

My observations agree very well with Perkin's, although the specimen examined by him boiled between 29° and 32°. It was prepared by Schorlemmer, and, no doubt, contained some normal pentane, the specific gravity of which differs but slightly from that of isopentane.

*Critical Constants.*

| | | Fraction A. | | Fraction B. | |
|---|---|---|---|---|---|
| | | Temperature. | Pressure. millim. | Temperature. | Pressure. millim. |
| | | ° | | ° | |
| With Aniline vapour as jacket | (1) | 187·75 | 25020 | 187·75 | 25000 |
| | (2) | 187·8 | 25020 | | |
| ,, Quinoline ,, ,, | (1) | 187·85 | 25030 | 187·85 | 25020 |
| | (2) | 187·9 | 25020 | | |

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* *Beiblätter*, ix. p. 697.

† Landolt and Jahn calculate the specific gravity at 0° as 0·64116.

The mean values are :—

| | |
|---|---|
| Critical temperature . . . | 187°·8 |
| Critical pressure . . . . | 25015 millim. |

The sample prepared by Thomas and myself gave the following results :—

| | |
|---|---|
| Critical temperature . . . | 187°·8. |
| Critical pressure . . . . | 25030 millim. |

The critical volume of a gram, calculated by the method of Cailletet and Mathias from the mean densities of liquid and saturated vapour at lower temperatures, is 4·266 cub. centim.

*Critical Constants by other Observers.*

| | Temperature. | Pressure. millim. |
|---|---|---|
| | ° | |
| Schmidt . . . | 193·0 | |
| Pawlewski . . | 194·8 | |
| Altschul . . . | 187·1 | 25300 |

It may be pointed out that Schmidt's sample of isopentane contained some normal pentane, which would raise the critical temperature, and that Pawlewski's observations of critical temperature are in most cases somewhat higher than mine. On the other hand, those of Altschul agree well in the few cases that can be compared. They are given in the table below :—

| | ALTSCHUL. | | YOUNG. | |
|---|---|---|---|---|
| | Temperature. | Pressure. | Temperature. | Pressure. |
| | ° | atm. | ° | atm. |
| Normal Hexane ... | 234·5 | 30·0 | 235·0 | 29·76 |
| Benzene.............. | 290·5 | 50·1 | 288·5 | 47·9 |
| Chlorobenzene ...... | 362·2 | ...... | 359·3 * | ...... |

* Corrected for error in the boiling-point of mercury.

### *Vapour-Pressures at Low Temperatures.*

The vapour-pressures at temperatures below the boiling-point under atmospheric pressure were determined by the dynamical method of Ramsay and Young (Trans. Chem. Soc. xlvii. p. 43).

For temperatures below 0° a thermometer by Warmbrunn, Quilitz, & Co. of Berlin was employed; it had been standardized by the Physikalisch-Technische Reichsanstalt. The effect of alteration of pressure on the readings of the thermometer was ascertained and allowed for, and the very small correction for the heated column of mercury in the stem of the thermometer was also applied.

The logarithms of the vapour-pressures were mapped against the temperatures, and the values at each ten degrees were read from the curve. The observed pressures are given in the table below, and the pressures at even temperatures in the table on p. 613.

Vapour-Pressures at Low Temperatures.

| Temperature. | Pressure. | Temperature. | Pressure. | Temperature. | Pressure. | Temperature. | Pressure. |
|---|---|---|---|---|---|---|---|
| Sample A (1). | | | | | | | |
| ° | millim. | ° | millim. | ° | millim. | ° | millim. |
| −31·83 | 52·7 | −26·18 | 71·85 | −12·86 | 143·4 | −3·48 | 221·6 |
| −31·38 | 53·95 | −23·59 | 83·2 | −12·71 | 144·15 | −0·81 | 249·7 |
| −30·29 | 57·5 | −23·01 | 84·9 | − 9·45 | 168·4 | +0·10 | 259·1 |
| −28·88 | 62·3 | −20·45 | 98·0 | − 6·53 | 193·05 | | |
| −26·53 | 71·0 | −16·13 | 122·1 | − 6·45 | 193·5 | | |
| Sample A (2). | | | | | | | |
| +2·55 | 290·5 | 11·65 | 422·5 | 20·9 | 587·6 | | |
| 5·6 | 330·8 | 14·9 | 473·3 | 23·35 | 642·5 | | |
| 9·0 | 377·3 | 17·95 | 529·4 | 25·95 | 705·2 | | |
| Sample B (1). | | | | | | | |
| −31·08 | 54·75 | −25·91 | 73·45 | −14·24 | 134·05 | −4·82 | 208·85 |
| −29·47 | 60·1 | −22·33 | 88·9 | −10·38 | 161·35 | −2·44 | 232·3 |
| −29·04 | 61·75 | −18·06 | 110·95 | − 7·01 | 189·35 | +0·07 | 259·4 |
| Sample B (2). | | | | | | | |
| +0·4 | 262·6 | 10·05 | 389·7 | 19·05 | 550·7 | 26·2 | 712·0 |
| 2·75 | 302·0 | 13·2 | 441·1 | 21·9 | 607·1 | 28·05 | 760·55 |
| 6·65 | 341·3 | 16·35 | 499·8 | 24·2 | 661·2 | | |

### *Vapour-Pressures at High Temperatures.*

The volumes of a gram of liquid and saturated vapour and the vapour-pressures at temperatures above the ordinary boiling-point were determined with the pressure apparatus employed in my previous researches. The tube containing the isopentane was heated by the vapour of pure liquids boiling under known pressures (Ramsay and Young, Trans. Chem. Soc. xlvii. p. 640; Young, ibid. lv. p. 483). The temperatures are those of an air-thermometer. The pressures, determined by means of air-gauges, are corrected for (1) the difference in height of the columns of mercury in the air-gauge and volume-tube; (2) the expansion of the heated column of mercury; (3) the pressure of the column of isopentane; (4) the deviation of air from Boyle's law, as determined by Amagat.

There were eight series of determinations, and, as a rule, four readings of pressure were taken at each temperature, the volume being altered as much as possible. The individual readings agreed very well together, and the mean values only are given in the following table (p. 613).

The constants for Biot's formula

$$\log p = a + b\alpha^t + c\beta^t$$

are given below.

$$a = 11{\cdot}371605\,;$$

$$b = -8{\cdot}030139, \quad \log b = 0{\cdot}9047231,$$

$$c = -1{\cdot}575796, \quad \log c = 0{\cdot}1975000\,;$$

$$\log \alpha = \bar{1}{\cdot}99968451,$$

$$\log \beta = \bar{1}{\cdot}99484097,$$

$$t = t^\circ\,\text{C.} + 30.$$

The vapour-pressures calculated from Biot's formula are also given in the table.

Table of Vapour-Pressures.

| Temperature. | Dynamical Method. | I. A. | II. B. | III. A. | IV. A. | V. B. | VI. A. | VII. A. | VIII. A. | Calculated. |
|---|---|---|---|---|---|---|---|---|---|---|
| −30 | 58·55 | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | 58·30 |
| −20 | 100·0 | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | 100·06 |
| −10 | 164·05 | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | 163·95 |
| 0 | 257·35 | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | 257·74 |
| 10 | 390·4 | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | 390·52 |
| 20 | 572·2 | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | 572·59 |
| 30 | 815·5 | ...... | ...... | ...... | 820 | ...... | ...... | ...... | 822 | 815·34 |
| 40 | ...... | ...... | ...... | ...... | 1137 | ...... | ...... | ...... | 1144 | 1131·1 |
| 50 | ...... | ...... | 1535 | ...... | ...... | ...... | 1536 | 1536 | ...... | 1533·2 |
| 60 | ...... | ...... | 2037 | ...... | ...... | ...... | 2036 | ...... | ...... | 2035·6 |
| 70 | ...... | 2657 | 2656 | ...... | ...... | ...... | 2657 | ...... | ...... | 2653·0 |
| 80 | ...... | ...... | 3385 | 3381 | ...... | ...... | ...... | ...... | ...... | 3400·8 |
| 90 | ...... | 4283 | 4281 | 4280 | ...... | ...... | ...... | ...... | ...... | 4295·6 |
| 100 | ...... | ...... | 5347 | 5344 | ...... | ...... | ...... | ...... | ...... | 5354·5 |
| 110 | ...... | ...... | 6583 | 6581 | 6586 | 6585 | ...... | ...... | ...... | 6596·1 |
| 120 | ...... | ...... | 8020 | 8020 | 8016 | 8016 | ...... | ...... | ...... | 8039·9 |
| 130 | ...... | ...... | 9685 | 9687 | 9682 | 9682 | ...... | ...... | ...... | 9706·7 |
| 140 | ...... | 11630 | 11640 | 11640 | 11630 | 11630 | ...... | ...... | ...... | 11620 |
| 150 | ...... | 13800 | 13800 | 13810 | 13800 | ...... | ...... | ...... | ...... | 13804 |
| 160 | ...... | ...... | 16320 | 16320 | 16320 | ...... | ...... | ...... | ...... | 16285 |
| 170 | ...... | ...... | 19110 | 19120 | ...... | ...... | ...... | ...... | ...... | 19094 |
| 176 | ...... | ...... | ...... | 20970 | ...... | ...... | ...... | ...... | ...... | 20950 |
| 180 | ...... | ...... | 22270 | ...... | ...... | ...... | ...... | ...... | ...... | 22262 |
| 183 | ...... | ...... | ...... | 23310 | ...... | ...... | ...... | ...... | ...... | 23288 |
| 185 | ...... | ...... | 24000 | ...... | ...... | ...... | ...... | ...... | ...... | 23992 |
| 186 | ...... | ...... | ...... | 24370 | ...... | ...... | ...... | ...... | ...... | 24350 |
| 187 | ...... | ...... | 24730 | ...... | ...... | ...... | ...... | ...... | ...... | 24713 |
| 187·4 | ...... | ...... | ...... | 24880 | ...... | ...... | ...... | ...... | ...... | ...... |
| Critical 187·8 | ...... | ...... | 25010 | 25025 | 25020 | ...... | ...... | ...... | ...... | 25005 |

### *Volumes of a Gram of Liquid and Vapour.*

In the first three series the mass of substance was determined by observing the volumes of liquid at a series of temperatures. These volumes were mapped against the temperatures and curves drawn through the points. The values at 0°, 13°·45, and 14°·4 were read off and were multiplied by the specific gravities at those temperatures.

For Series IV. and V. comparisons were made of the volumes of liquid and also of unsaturated vapour at a large number of different temperatures and pressures with those read from the curves constructed from the data obtained in the previous series.

The mass of substance in Series VI. was similarly ascertained by comparison of volumes with those read from the isothermals of Series IV. and V. at the same temperatures and pressures. So also with the remaining series, the calculated mass depended in each case on the data obtained in the preceding series.

A series of determinations of the volumes of unsaturated vapour was afterwards made by Thomas and myself in a modified Hofmann's apparatus, the mass of isopentane being determined by direct weighing. The smallest volumes of a gram in this series were nearly the same as the largest in Series VIII. with the pressure apparatus; and as the isothermals constructed from the observations with the modified Hofmann's apparatus were quite continuous with those of Series VIII., the determination of mass in this series—which might be charged with the cumulative errors of each preceding determination—was shown to be accurate.

### *Orthobaric Volumes of a Gram of Liquid.*

The volumes at 0°, 13°·45, and 14°·4 were calculated from the specific gravities at the same temperatures. The observations were made under atmospheric pressure, but the correction of the volumes to the true vapour-pressures has not been made, as the difference would be inappreciable.

In the pressure apparatus the volumes of liquid up to 130° were read directly, the vapour being completely condensed and the pressure made as nearly as possible equal to the vapour-pressure. At and above 140° the liquid is very compressible, and the volumes were therefore calculated from a series of readings of the volumes of vapour and of the total volume of liquid and saturated vapour at each temperature by the method described in the Trans. Chem. Soc. lxiii. p. 1200.

The volumes of liquid (when all vapour is condensed) and of saturated vapour (when all liquid is evaporated) may also be ascertained very simply by the following graphical method :—

Let the total volume (liquid and uncondensed vapour) at any reading $= \mathrm{V}$.
„ volume of saturated vapour at the same time $= v$.
„ „ of liquid when all condensed $= \mathrm{A}$.
„ „ of saturated vapour when all evaporated $= \mathrm{B}$.
„ ratio of the specific volume of saturated vapour to that of liquid $= \mathrm{R}$.
„ volume of liquid (*i.e.* $\mathrm{V}-v) = \mathrm{A}-n$.

Then the volume of vapour, $v = n\mathrm{R}$,

and the total volume, $\mathrm{V} = \mathrm{A} - n + n\mathrm{R}$,

or $\mathrm{V} = \mathrm{A} + n(\mathrm{R}-1)$.

Call $\dfrac{\mathrm{R}-1}{\mathrm{R}} = c$;

then

$$\mathrm{V} = \mathrm{A} + \frac{\mathrm{R}-1}{\mathrm{R}} . n\mathrm{R}$$
$$= \mathrm{A} + cv.$$

If we map the total volumes, ($\mathrm{V}_1$, $\mathrm{V}_2$, &c.) against the volumes of saturated vapour ($v_1$, $v_2$, &c.) and draw a straight line through the points, then when

$$v = 0, \quad \mathrm{V} = \mathrm{A},$$

and when $v = \mathrm{V}$, $\mathrm{V} = \mathrm{B}$.

Again, let the volumes of saturated vapour $v$ at any reading $= \mathrm{B} - m$.

Also call the volume of liquid $v'$ when the total volume $= \mathrm{V}$, so that $v' = \dfrac{m}{\mathrm{R}}$.

Then the total volume, $\mathrm{V} = \mathrm{B} - m + \dfrac{m}{\mathrm{R}}$

$$= \mathrm{B} - m . \frac{\mathrm{R}-1}{\mathrm{R}} .$$

Make $R-1=c'$,

then

$$V=B-(R-1)\cdot\frac{m}{R}$$

$$=B-c'v'.$$

If we map the total volumes $V_1$, $V_2$, &c., against the volumes of liquid $v_1'$, $v_2'$, &c., then when

$$v'=0,\quad V=B,$$

and when $v'=V,\quad V=A.$

The first method is better suited for the volumes of saturated vapour, the second for the volumes of liquid.

The orthobaric volumes of a gram of liquid, calculated from the experimental data, and also those read from the curves constructed from the observed values are given in the following table :—

Orthobaric Volumes of a Gram of Liquid.

| Temp. | From Specific Gravities. | Series I. | Series II. | Series III. | Mean. | From Curves. |
|---|---|---|---|---|---|---|
| | c. c. | c. c. | c. c. | c. c. | c. c. | c. c. |
| 0° | 1·5644 | ...... | ...... | ...... | 1·5644 | 1·5644 |
| 10 | ...... | 1·5885 | ...... | ...... | 1·5885 | 1·5885 |
| 13·45 | 1·5971 | ...... | ...... | ...... | 1·5971 | 1·5972* |
| 14·4 | 1·5996 | ...... | ...... | ...... | 1·5996 | 1·5996* |
| 20 | ...... | 1·6140 | ...... | ...... | 1·6140 | 1·6141 |
| 30 | ...... | 1·6415 | 1·642 | ...... | 1·6415 | 1·6413 |
| 40 | ...... | 1·6700 | 1·670 | ...... | 1·6700 | 1·6700 |
| 50 | ...... | 1·7005 | 1·700 | ...... | 1·7005 | 1·7005 |
| 60 | ...... | 1·7330 | 1·734 | ...... | 1·7335 | 1·7329 |
| 70 | ...... | 1·7680 | 1·768 | ...... | 1·7680 | 1·7679 |
| 80 | ...... | 1·3045 | 1·806 | ...... | 1·8050 | 1·8055 |
| 90 | ...... | 1·8475 | 1·847 | ...... | 1·8475 | 1·8475 |
| 100 | ...... | 1·8945 | 1·894 | ...... | 1·8945 | 1·8940 |
| 110 | ...... | 1·9455 | 1·945 | ...... | 1·9455 | 1·9455 |
| 120 | ...... | 2·0040 | 2·003 | ...... | 2·0035 | 2·0037 |
| 130 | ...... | 2·0720 | 2·072 | ...... | 2·0720 | 2·0720 |
| 140 | ...... | 2·1525 | 2·156 | 2·153 | 2·1540 | 2·1530 |
| 150 | ...... | 2·2490 | 2·252 | 2·248 | 2·2495 | 2·2500 |
| 160 | ...... | ...... | 2·378 | 2·377 | 2·3775 | 2·3780 |
| 170 | ...... | ...... | 2·555 | 2·555 | 2·5550 | 2·5550 |
| 176 | ...... | ...... | ...... | 2·707 | 2·7070 | 2·7070 |
| 180 | ...... | ...... | 2·859 | ...... | 2·8590 | 2·8580 |
| 183 | ...... | ...... | ...... | 3·020 | 3·0200 | 3·0200 |
| 185 | ...... | ...... | 3·183 | ...... | 3·1830 | 3·1830 |
| 186 | ...... | ...... | ...... | 3·303 | 3·3030 | 3·3020 |
| 187 | ...... | ...... | 3·500 | ...... | 3·5000 | 3·5000 |
| 187·4 | ...... | ...... | ...... | 3·622 | 3·6220 | 3·6220 |
| Critical 187·8 | ...... | ...... | ...... | ...... | ...... | 4·2660† |

* From densities calculated from the formula

$$D_t=0{\cdot}63923-0{\cdot}0_3958\,t-0{\cdot}0_513\,t^2.$$

† By the method of Cailletet and Mathias.

### *Orthobaric Volumes of a Gram of Vapour.*

The volumes of saturated vapour were determined by three different methods :—

I. With the pressure apparatus from a series of four readings of the total volume of liquid and uncondensed vapour and of the vapour at each temperature at and above 110°.

This method (Trans. Chem. Soc. lxiii. p. 1200) gives very good results at high temperatures, but is not accurate when the ratio of the volume of a gram of saturated vapour to that of liquid is large. It has been described and recommended by Amagat (*Compt. Rend.* cxiv. p. 1093).

The graphical method described on p. 614 may be employed to ascertain the volume of saturated vapour when all the liquid is evaporated, and this, divided by the mass of substance in the tube, gives the volume of a gram of saturated vapour.

II. By heating a known quantity of liquid in a graduated sealed tube (Young, Trans. Chem. Soc. lix. p. 37 ; lxiii. p. 1201).

The method was originally devised for the purpose of determining the specific volumes (both as liquid and as saturated vapour) of liquids that attack mercury, but it has been found very convenient—in a modified and simpler form—for the determination of the volumes of a gram of the saturated vapours of ordinary substances whose specific volumes, as liquid, are known. The form of the sealed tube, the method of filling it, and the arrangements for heating it, are the same as are described in the paper referred to (vol. lix. pp. 40 and 41), but it is, of course, unnecessary to keep the lower part of the tube cool, and the water-jacket below is therefore not required.

The tube A is at first placed in the position shown in the diagram (fig. 1), with the level of the liquid in the tube below the condensed liquid B in the jacket. The liquid in the bulb C is then boiled—with the pressure rather lower than that corresponding to the lowest temperature required—and when the vapour has reached the condenser* D the sealed tube is slowly pushed up through the indiarubber tube E until the whole of the liquid in it is well above the surface of the condensed liquid B. The indiarubber tube should be kept under water for a day or two before being used, and should be surrounded by water until the sealed tube has been pushed up into its

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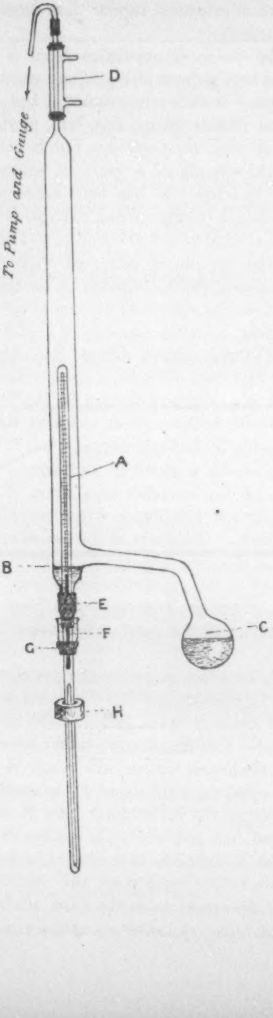
* For liquids boiling above 160° a condenser is not required.

Fig. 1.



final position, otherwise considerable difficulty may be experienced in moving the sealed tube through it. The little glass tube F, filled with water and provided with a very short indiarubber tube G moving easily over the sealed tube, serves to keep the indiarubber tube E moist. The sealed tube is easily centred by means of a perforated cork H, held in position by a clamp and retort-stand. After the tube is in position the pressure under which the liquid in C is boiling is slowly raised until it corresponds to the required temperature, and a reading of the height of the liquid is then taken. A second reading is then taken after two or three minutes, and if the volume of liquid is smaller readings are taken from time to time until constancy is attained.

At moderate temperatures the volume of liquid should become constant almost immediately, but near the critical point the evaporation of the liquid becomes much slower, and this is especially the case if any appreciable amount of air or permanent gas is left in the tube. The amount of permanent gas must be exceedingly small, otherwise the results obtained are found to be inaccurate, owing probably to partial condensation of the vapour on the sides of the tube.

After the reading has become constant the pressure is again slowly raised—care being taken not to drive down the vapour below the top of the sealed tube—until the next temperature is reached.

If the top of the tube is cooled, condensation takes place in it, and there is danger of liquid remaining in contact with the walls of the tube, and of the apparent volume of liquid being therefore too small.

For the same reason it is advisable to begin treating the tube in the manner described, for if the tube were placed in its final position at the beginning of the experiment the liquid would boil and would collect at the top of the tube.

III. From the isothermals; the points of intersection of the curves representing the unsaturated vapour with the horizontal lines of vapour-pressure give the volumes of saturated vapour.

The logarithms of the volumes were mapped against the temperature, and the smoothed values read from the curve. These are given in the following table together with the values obtained by the three methods described above.

Orthobaric Volumes of a Gram of Vapour.

| Temperature. | In Pressure Apparatus. | | | | Sealed Tube Method. | | From Isothermal Curves. | Mean. | From Curve. |
|---|---|---|---|---|---|---|---|---|---|
| | II. | III. | IV. | V. | I. | II. | | | |
| ° | c. c. | c. c. | c. c. | c. c. | c. c. | c. c. | c. c. | c. c. | c. c. |
| 10·8 | ...... | ...... | ...... | ...... | ...... | ...... | 591·5* | 591·5 | |
| 10 | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | 607·5 |
| 20 | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | 424·0 |
| 30 | ...... | ...... | ...... | ...... | 301 | ...... | 304·5 | 303 | 303·0 |
| 40 | ...... | ...... | ...... | ...... | 224 | ...... | 223·0 | 223·5 | 223·2 |
| 50 | ...... | ...... | ...... | ...... | 168·5 | ...... | 168·0 | 168·2 | 167·6 |
| 60 | ...... | ...... | ...... | ...... | 128·0 | ...... | 128·0 | 128·0 | 127·9 |
| 70 | ...... | ...... | ...... | ...... | 98·4 | ...... | 99·00 | 98·7 | 98·9 |
| 80 | ...... | ...... | ...... | ...... | 77·7 | ...... | 77·95 | 77·8 | 77·9 |
| 90 | ...... | ...... | ...... | ...... | 61·8 | ...... | 61·87 | 61·85 | 61·85 |
| 100 | ...... | ...... | ...... | ...... | 49 65 | ...... | 49·35 | 49·5 | 49·45 |
| 110 | ...... | ...... | 38·9 | 39·6 | 39·85 | 40·2 | 39·83 | 39·7 | 39·80 |
| 120 | ...... | ...... | 32·3 | 32·3 | ...... | 32·6 | 32·20 | 32·35 | 32·20 |
| 130 | ...... | ...... | 26·05 | 26·05 | ...... | 26·3 | 26·10 | 26·10 | 26·10 |
| 140 | 21·00 | 21·20 | 21·10 | 21·05 | ...... | 21·15 | 21·15 | 21·10 | 21·15 |
| 150 | 17·13 | 17·18 | 17·13 | ...... | ...... | 17·19 | 17·14 | 17·15 | 17·14 |
| 160 | 13·69 | 13·71 | 13·73 | ...... | ...... | 13·69 | 13·72 | 13·71 | 13·72 |
| 170 | 10·73 | 10·73 | ...... | ...... | ...... | 10·72 | 10·73 | 10·73 | 10·71 |
| 176 | ...... | 9·075 | ...... | ...... | ...... | ...... | 9·07 | 9·07 | 9·08 |
| 180 | 7·952 | ...... | ...... | ...... | ...... | 7·955 | 7·95 | 7·952 | 7·95 |
| 183 | ...... | 7·045 | ...... | ...... | ...... | ...... | 7·035 | 7·040 | 7·05 |
| 185 | 6·348 | ...... | ...... | ...... | ...... | 6·375 | 6·35 | 6·354 | 6·355 |
| 186 | ...... | 5·963 | ...... | ...... | ...... | 5·963 | ...... | 5·963 | 5·965 |
| 187 | 5·453 | ...... | ...... | ...... | ...... | ...... | ...... | 5·453 | 5·455 |
| 187·4 | ...... | 5·126 | ...... | ...... | ...... | ...... | ...... | 5·126 | 5·125 |
| 187·8 † | ...... | ...... | ...... | ...... | ...... | ...... | ...... | 4·266 | 4·266 |

* From determinations in the modified Hofmann's apparatus (Young and Thomas).

† By the method of Cailletet and Mathias.

*Volumes of a Gram of Liquid and of Unsaturated Vapour.*

Eight series of determinations were made in the pressure apparatus.

| Series. | Specimen of Isopentane employed. | Mass of Isopentane. gram. | Data obtained. |
|---|---|---|---|
| I. | A | 0·30244 | Volumes of liquid up to 150°. |
| II. | A | 0·09504 | Volumes of liquid to critical point; a few volumes of unsaturated vapour at and above 176°; volumes above the critical point to 280°. |
| III. | B | 0·11516 | |
| IV. | A | 0·03405 | Volumes of unsaturated vapour from 140° to critical point; volumes above critical point to 280°. |
| V. | B | 0·03010 | |
| VI. | B | 0·00888 | Volumes of vapour at and above 90°. |
| VII. | B | 0·003743 | ,, ,, ,, 50°. |
| VIII. | B | 0·001225 | ,, ,, ,, 30°. |

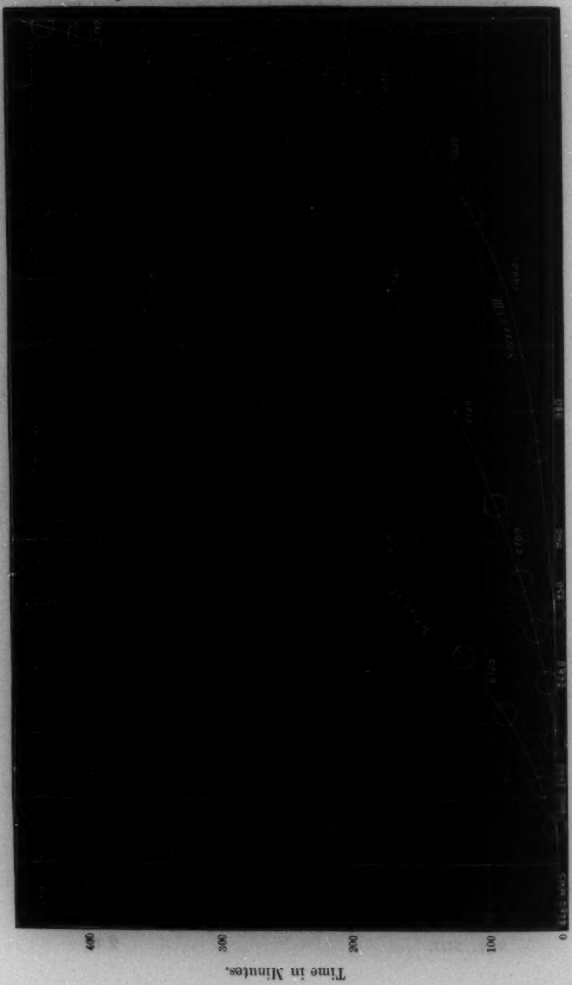
In Series VI. to VIII. the volumes were determined at temperatures up to 280°.

*Correction of Pressures.*—In addition to the corrections for the difference in height of the columns of mercury, the expansion of the heated column, and the deviation of air from Boyle's law, there is another which is of importance at the highest temperatures, but is somewhat difficult to estimate. This is the correction for the vapour-pressure of mercury.

It has been proved experimentally that the vapour of mercury penetrates a column of liquid over it with extreme slowness, and no correction has therefore been applied in the measurement of the vapour-pressure of isopentane or even of other substances with much higher critical temperatures.

When, however, there is only gas over the mercury the vapour of the metal diffuses slowly through it, the rate of diffusion increasing as the pressure of the gas is diminished. Even with the smallest quantity of isopentane at its largest volume, when the pressure of the gas was little over an atmosphere, the maximum pressure at 280° was not attained until after about four hours' heating. It is quite certain that with the larger quantities of substance a much longer time would be required, and as it was impossible, owing to other work, to keep the tube continuously heated for more than four or five hours, the only plan was to make an approximate estimate of the pressure exerted by the mercury-vapour.

Fig. 2.



In the determinations of the volumes of a gram of unsaturated vapour the readings were always taken with diminishing volume, and at the higher temperatures the tube was heated for several hours with the substance at its largest volume. Readings were taken at short intervals, and were plotted against the time so as to get an idea of the rate of increase of the pressure.

The time-curves at 280° for the last three series are given in fig. 2. It will be seen that in Series VIII. the rise of pressure was at first very rapid, but that after two hours it had become very slow, and that the pressure after four hours was practically constant. The vapour-pressure of mercury at 280° is 158 millim., and the measured rise of pressure was 85 millim. The difference is, no doubt, due to the fact that the readings could not be begun until after the tube had been heated for some little time.

In Series VII. the rise was at first not quite so rapid as in Series VIII., and it was not until the tube had been heated for six hours that approximate constancy was attained. In this case the measured rise of pressure was 110 millim.

In Series VI. the rate of increase of pressure was much slower than in the later series, and the pressure was far from constant after five hours; the last reading was 78 millim. higher than the first.

It appears then that with the two smallest quantities of isopentane the mercury-vapour, after a sufficient time, exerted its full pressure, but that with the larger quantities the maximum pressure was not attained; also that when there is a column of liquid over the mercury no appreciable pressure is exerted by the vapour of the metal.

It was assumed that in Series II. and III. the vapour-pressure of the mercury amounted to one fourth of its maximum value; in Series IV. and V. to one half, in Series VI. to three quarters, and that in the last two series the full vapour-pressure was exerted*.

The time-curves for Series VII. and VIII. show that the error caused by assuming that the mercury-vapour exerted its full pressure cannot amount to more than one or two millim. in Series VIII., and to three or four millim. in Series VII.; and it is very unlikely that in the other series the error can amount to so much as a fourth of the maximum vapour-pressure of mercury. In Series VI., for instance, it is certain that the actual pressure exerted by the mercury-vapour was greater than half and less than the whole maximum pressure. At 280° the vapour-pressure of mercury is 158 millim., the rise of pressure actually measured 78 millim., and the pressure assumed to be exerted by the mercury vapour 118 millim. The error is therefore considerably less than 40 millim. At the largest volume the uncorrected pressure was 6174 millim., and the extreme error would therefore be under 0·7 per cent.

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* In Series VII. the tube was heated for six hours at 250° and 280°, and for over four hours at 200° and 220°.

This is by far the worst case, for the vapour-pressure of mercury diminishes rapidly with fall of temperature, whilst with the larger quantities of isopentane the total pressure is proportionately increased. Thus, at 260° (Series VI.) the extreme error, calculated in the same way, would be 0·4 per cent., at 240° 0·25 per cent., at 200° 0·08 per cent., whilst at 280° (Series V.) it would be just over 0·2 per cent., and at 280° (Series III.) less than 0·1 per cent.

At temperatures above 150° the jacketing tube was protected from draughts and from loss of heat by radiation by an outer cylindrical glass tube about 8 or 10 millim. wider than the jacketing tube, the space at the top between the two tubes being closed by asbestos to prevent the upward current of air which would otherwise be formed. It was still possible that the tube containing the isopentane lost some heat by radiation and that its temperature was therefore a little too low.

In order to find whether this was the case the outer glass tube was covered with sheet asbestos after the eleventh reading at 280° in Series VIII. had been taken. It will be seen that the last two readings, with the tube doubly protected, fall accurately on the time-curve constructed from the previous readings.

Similar experiments had been made with the larger quantities of isopentane, but in no case was any alteration produced by covering the outer tube with asbestos. It may therefore be concluded that up to 280° the cylindrical glass tube affords sufficient protection from radiation.

The experimental results are given in the following Tables:—

## *Volumes of a Gram of Liquid and of Unsaturated Vapour.*

### SERIES I.

| Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. |
|---|---|---|---|---|---|---|---|---|
| 10°...... | 790 | 1·5890 | 50°...... | 43960 | 1·6710 | 100° ... | 33240 | 1·8500 |
| | 4030 | 1·5870 | (*cont.*) | 50660 | 1·6675 | (*cont.*) | 38960 | 1·8420 |
| | 7960 | 1·5850 | | 54840 | 1·6655 | | 44050 | 1·8355 |
| | 11520 | 1·5840 | 60°...... | 2040 | 1·7330 | | 50760 | 1·8270 |
| | 15140 | 1·5825 | | 5300 | 1·7305 | | 54950 | 1·8225 |
| | 20070 | 1·5810 | | 8090 | 1·7275 | 110° ... | 6580 | 1·9455 |
| | 26310 | 1·5780 | | 11690 | 1·7245 | | 8460 | 1·9405 |
| | 32720 | 1·5755 | | 15370 | 1·7215 | | 11740 | 1·9335 |
| | 38350 | 1·5735 | | 20360 | 1·7180 | | 15420 | 1·9260 |
| | 43360 | 1·5715 | | 26680 | 1·7125 | | 20420 | 1·9170 |
| | 49970 | 1·5685 | | 33180 | 1·7080 | | 26750 | 1·9050 |
| | 54100 | 1·5675 | | 38870 | 1·7035 | | 33260 | 1·8945 |
| 15°·6 ... | 810 | 1·6025 | | 43960 | 1·7000 | | 38990 | 1·8845 |
| | 4100 | 1·6015 | | 50650 | 1·6955 | | 44100 | 1·8765 |
| | 8110 | 1·5995 | | 54840 | 1·6920 | | 50800 | 1·8670 |
| | 11720 | 1·5975 | 70°...... | 2690 | 1·7680 | | 54990 | 1·8610 |
| | 15420 | 1·5960 | | 5300 | 1·7660 | 120° ... | 8020 | 2·0040 |
| | 20430 | 1·5945 | | 8100 | 1·7620 | | 10310 | 1·9970 |
| | 26760 | 1·5915 | | 11700 | 1·7590 | | 15400 | 1·9835 |
| | 33300 | 1·5885 | | 15380 | 1·7550 | | 20390 | 1·9705 |
| | 39040 | 1·5855 | | 20380 | 1·7515 | | 26700 | 1·9560 |
| | 44150 | 1·5835 | | 26710 | 1·7450 | | 33200 | 1·9420 |
| | 50880 | 1·5820 | | 33210 | 1·7395 | | 38900 | 1·9305 |
| | 55080 | 1·5795 | | 38920 | 1·7345 | | 43990 | 1·9215 |
| 30°...... | 820 | 1·6415 | | 44020 | 1·7310 | | 50700 | 1·9105 |
| | 4110 | 1·6385 | | 50720 | 1·7260 | | 54880 | 1·9035 |
| | 8110 | 1·6365 | | 54910 | 1·7220 | 130° ... | 9670 | 2·0720 |
| | 11730 | 1·6345 | 80°...... | 3390 | 1·8045 | | 11740 | 2·0640 |
| | 15410 | 1·6325 | | 5620 | 1·8020 | | 15420 | 2·0505 |
| | 20430 | 1·6300 | | 8090 | 1·7990 | | 20430 | 2·0330 |
| | 26770 | 1·6265 | | 11690 | 1·7955 | | 26750 | 2·0150 |
| | 33300 | 1·6235 | | 15360 | 1·7910 | | 33260 | 1·9975 |
| | 39020 | 1·6205 | | 20360 | 1·7855 | | 38970 | 1·9835 |
| | 44130 | 1·6185 | | 26880 | 1·7795 | | 44070 | 1·9710 |
| | 50860 | 1·6155 | | 33200 | 1·7730 | | 50770 | 1·9570 |
| | 55050 | 1·6135 | | 38910 | 1·7675 | | 54950 | 1·9485 |
| 40°...... | 1110 | 1·6700 | | 44000 | 1·7625 | 140° ... | 11640 | 2·1525 |
| | 4110 | 1·6680 | | 50700 | 1·7565 | | 13030 | 2·1450 |
| | 8100 | 1·6660 | | 54890 | 1·7525 | | 15360 | 2·1320 |
| | 11710 | 1·6630 | 90°...... | 4290 | 1·8475 | | 20330 | 2·1100 |
| | 15390 | 1·6610 | | 6000 | 1·8450 | | 26610 | 2·0835 |
| | 20400 | 1·6580 | | 8110 | 1·8420 | | 33070 | 2·0615 |
| | 26740 | 1·6535 | | 11710 | 1·8365 | | 38740 | 2·0440 |
| | 33250 | 1·6505 | | 15400 | 1·8315 | | 43800 | 2·0290 |
| | 38980 | 1·6470 | | 20400 | 1·8255 | | 50460 | 2·0120 |
| | 44070 | 1·6445 | | 26720 | 1·8170 | | 54620 | 2·0015 |
| | 50790 | 1·6415 | | 33230 | 1·8090 | 150° ... | 13800 | 2·2490 |
| | 54990 | 1·6385 | | 38950 | 1·8025 | | 15370 | 2·2365 |
| 50°...... | 1530 | 1·7005 | | 44040 | 1·7975 | | 17740 | 2·2190 |
| | 5290 | 1·6975 | | 50750 | 1·7910 | | 20340 | 2·2010 |
| | 8080 | 1·6950 | | 54940 | 1·7860 | | 26620 | 2·1645 |
| | 11680 | 1·6925 | 100° ... | 5360 | 1·8945 | | 33100 | 2·1335 |
| | 15360 | 1·6900 | | 8130 | 1·8900 | | 38780 | 2·1110 |
| | 20350 | 1·6870 | | 11730 | 1·8830 | | 43840 | 2·0920 |
| | 26670 | 1·6830 | | 15410 | 1·8765 | | 50520 | 2·0700 |
| | 33170 | 1·6785 | | 20410 | 1·8690 | | 54680 | 2·0580 |
| | 38870 | 1·6740 | | 26740 | 1·8590 | | | |

## SERIES II.

| Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. |
|---|---|---|---|---|---|---|---|---|
| 30° … | 800 | 1·642 | 130° … | 36770 | 1·989 | 187°·8 | 29110 | 2·791 |
| | 7920 | 1·637 | (*cont.*) | 47250 | 1·966 | (Critical) | 31330 | 2·700 |
| | 15180 | 1·632 | 140° … | 11640 | 2·156 | (*cont.*) | 34600 | 2·608 |
| | 31400 | 1·624 | | 15230 | 2·133 | | 39480 | 2·517 |
| | 46780 | 1·617 | | 25540 | 2·090 | | 46740 | 2·426 |
| 40° … | 1100 | 1·670 | | 36620 | 2·050 | 190° … | 25550 | 5·739 |
| | 7900 | 1·667 | | 46920 | 2·021 | | 25660 | 5·371 |
| | 15140 | 1·661 | 150° … | 13800 | 2·252 | | 25760 | 4·999 |
| | 31350 | 1·652 | | 17630 | 2·219 | | 25860 | 4·628 |
| | 46710 | 1·643 | | 25560 | 2·168 | | 25880 | 4·258 |
| 50° … | 1535 | 1·700 | | 36650 | 2·118 | | 25930 | 3·892 |
| | 7930 | 1·695 | | 46950 | 2·081 | | 26170 | 3·523 |
| | 15200 | 1·690 | 160° … | 16320 | 2·378 | | 26410 | 3·340 |
| | 31450 | 1·678 | | 17380 | 2·360 | | 26980 | 3·156 |
| | 46860 | 1·669 | | 19950 | 2·329 | | 28230 | 2·974 |
| 60° … | 2037 | 1·734 | | 25200 | 2·279 | | 29300 | 2·882 |
| | 7930 | 1·729 | | 31100 | 2·237 | | 30930 | 2·792 |
| | 15200 | 1·723 | | 36130 | 2·205 | | 33300 | 2·700 |
| | 31450 | 1·710 | | 40560 | 2·182 | | 36820 | 2·608 |
| | 46870 | 1·698 | | 46270 | 2·156 | | 41900 | 2·518 |
| 70° … | 2656 | 1·768 | 170° … | 19110 | 2·555 | | 49310 | 2·426 |
| | 7930 | 1·762 | | 20580 | 2·512 | 195° … | 27010 | 5·740 |
| | 15190 | 1·754 | | 25200 | 2·425 | | 27220 | 5·372 |
| | 31430 | 1·742 | | 31100 | 2·354 | | 27430 | 5·000 |
| | 46830 | 1·728 | | 36130 | 2·307 | | 27630 | 4·629 |
| 80° … | 3385 | 1·806 | | 40540 | 2·275 | | 27840 | 4·259 |
| | 8010 | 1·799 | | 46270 | 2·238 | | 28100 | 3·892 |
| | 15340 | 1·791 | 180° … | 22270 | 2·859 | | 28610 | 3·523 |
| | 31720 | 1·774 | | 23440 | 2·756 | | 29130 | 3·340 |
| | 47250 | 1·759 | | 27260 | 2·602 | | 30090 | 3·157 |
| 90° … | 4280 | 1·847 | | 31100 | 2·517 | | 31790 | 2·974 |
| | 8000 | 1·842 | | 36130 | 2·439 | | 33150 | 2·883 |
| | 15310 | 1·832 | | 40550 | 2·388 | | 35110 | 2·792 |
| | 31680 | 1·811 | | 46260 | 2·338 | | 37900 | 2·700 |
| | 47220 | 1·793 | 185° … | 24000 | 3·183 | | 41810 | 2·609 |
| 100° … | 5350 | 1·894 | | 24260 | 3·082 | | 47470 | 2·518 |
| | 7990 | 1·888 | | 25170 | 2·928 | 200° … | 28410 | 5·741 |
| | 15300 | 1·875 | | 27220 | 2·773 | | 28720 | 5·372 |
| | 31660 | 1·853 | | 29640 | 2·673 | | 29070 | 5·001 |
| | 47170 | 1·833 | | 32530 | 2·594 | | 29420 | 4·630 |
| 110° … | 6583 | 1·945 | | 36060 | 2·522 | | 29790 | 4·260 |
| | 8000 | 1·943 | | 40470 | 2·458 | | 30340 | 3·893 |
| | 15300 | 1·927 | | 46170 | 2·395 | | 31180 | 3·524 |
| | 31660 | 1·897 | 187°·8 | 24900 | 5·739 | | 31970 | 3·340 |
| | 47180 | 1·872 | (Critical) | 24960 | 5·371 | | 33240 | 3·157 |
| 120° … | 8020 | 2·003 | | 24990 | 4·999 | | 35450 | 2·975 |
| | 10190 | 1·999 | | 25000 | 4·628 | | 37070 | 2·883 |
| | 20340 | 1·970 | | 25010 | 4·258 | | 39380 | 2·792 |
| | 31690 | 1·946 | | 25020 | 3·892 | | 42490 | 2·701 |
| | 47200 | 1·916 | | 25070 | 3·523 | | 46880 | 2·609 |
| 130° … | 9685 | 2·072 | | 25190 | 3·339 | 210° … | 31170 | 5·742 |
| | 15340 | 2·048 | | 25650 | 3·156 | | 31740 | 5·374 |
| | 25710 | 2·019 | | 26670 | 2·974 | | 32350 | 5·002 |

## Series II. (*continued*).

| Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. |
|---|---|---|---|---|---|---|---|---|
| 210° ... | 33020 | 4·631 | 220° ... | 44830 | 3·250 | 240° ... | 47280 | 4·080 |
| (*cont.*) | 33790 | 4·261 | (*cont.*) | 46250 | 3·159 | (*cont.*) | 48020 | 3·989 |
| | 34830 | 3·894 | | 48060 | 3·067 | | 48800 | 3·897 |
| | 35500 | 3·710 | 230° ... | 35620 | 5·745 | 250° ... | 42020 | 5·748 |
| | 36420 | 3·525 | | 37700 | 5·377 | | 43600 | 5·379 |
| | 37730 | 3·341 | | 38860 | 5·004 | | 45420 | 5·007 |
| | 39640 | 3·158 | | 40160 | 4·633 | | 46480 | 4·821 |
| | 41000 | 3·066 | | 41780 | 4·263 | | 47510 | 4·635 |
| | 42710 | 2·975 | | 42800 | 4·079 | | 48150 | 4·543 |
| | 44980 | 2·884 | | 43970 | 3·896 | | 48760 | 4·450 |
| | 48020 | 2·793 | | 45460 | 3·712 | 260° ... | 44670 | 5·749 |
| 220° ... | 33910 | 5·744 | | 46230 | 3·619 | | 45570 | 5·565 |
| | 34700 | 5·375 | | 47290 | 3·526 | | 46490 | 5·381 |
| | 35570 | 5·003 | | 48420 | 3·435 | | 47550 | 5·194 |
| | 36540 | 4·632 | 240° ... | 39350 | 5·747 | | 48080 | 5·102 |
| | 37790 | 4·262 | | 40620 | 5·378 | | 48660 | 5·008 |
| | 38540 | 4·078 | | 42140 | 5·006 | 270° ... | 47380 | 5·751 |
| | 39410 | 3·895 | | 43840 | 4·634 | | 47880 | 5·659 |
| | 40440 | 3·711 | | 44870 | 4·449 | | 48400 | 5·566 |
| | 41750 | 3·525 | | 45980 | 4·264 | | 48830 | 5·475 |
| | 43620 | 3·342 | | | | | | |

## SERIES III.

| Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim. | Volume cub. cm. |
|---|---|---|---|---|---|---|---|---|
| 160° ... | 16320 | 2·377 | 176° ... | 27130 | 2·508 | 186° ... | 23900 | 7·177 |
| | 16420 | 2·375 | (*cont.*) | 29550 | 2·467 | | 24030 | 6·954 |
| | 18220 | 2·350 | | 32450 | 2·426 | | 24130 | 6·731 |
| | 20440 | 2·325 | | 35970 | 2·383 | | 24230 | 6·507 |
| | 23290 | 2·296 | | 40370 | 2·340 | | 24290 | 6·282 |
| | 27110 | 2·264 | | 46070 | 2·298 | | 24360 | 6·057 |
| | 32420 | 2·227 | | 49610 | 2·273 | | 24370 | 5·963 |
| | 38010 | 2·193 | | 53710 | 2·249 | | ,, | 3·303 |
| | 43000 | 2·170 | 183° ... | 23160 | 7·397 | | 25110 | 3·030 |
| | 49570 | 2·140 | | 23210 | 7·286 | | 26080 | 2·902 |
| | 53680 | 2·126 | | 23260 | 7·176 | | 27150 | 2·822 |
| 170° ... | 19120 | 2·555 | | 23300 | 7·064 | | 28300 | 2·757 |
| | 19290 | 2·545 | | 23310 | 7·045 | | 29560 | 2·704 |
| | 20470 | 2·513 | | ,, | 3·020 | 187°·4 | 24350 | 6·954 |
| | 23320 | 2·455 | | 23320 | 3·008 | | 24570 | 6·508 |
| | 27120 | 2·399 | | 24160 | 2·883 | | 24740 | 6·057 |
| | 32430 | 2·339 | | 25080 | 2·805 | | 24800 | 5·832 |
| | 38020 | 2·292 | | 27120 | 2·698 | | 24840 | 5·608 |
| | 43010 | 2·258 | | 29530 | 2·619 | | 24870 | 5·384 |
| | 49580 | 2·218 | | 32430 | 2·550 | | 24880 | 5·126 |
| | 53680 | 2·199 | | 35950 | 2·490 | | ,, | 3·622 |
| 176° ... | 20970 | 2·707 | | 40350 | 2·429 | | 24890 | 3·603 |
| | 21810 | 2·660 | | 46040 | 2·372 | | 24910 | 3·492 |
| | 23320 | 2·602 | | 49570 | 2·343 | | 24990 | 3·382 |
| | 25090 | 2·551 | | 53680 | 2·314 | | 25120 | 3·281 |

## Series III. (*continued*).

| Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. |
|---|---|---|---|---|---|---|---|---|
| 187°·4 (*cont.*) | 25256 | 3·205 | 190° … (*cont.*) | 25180 | 6·508 | 205° .. (*cont.*) | 29960 | 5·610 |
| | 26079 | 3·016 | | 25400 | 6·058 | | 30530 | 5·162 |
| | 26241 | 2·992 | | 25590 | 5·608 | | 31090 | 4·718 |
| | 27153 | 2·900 | | 25710 | 5·160 | | 31780 | 4·271 |
| | 27313 | 2·883 | | 25780 | 4·716 | | 32740 | 3·826 |
| | 28302 | 2·818 | | 25850 | 4·269 | | 33490 | 3·605 |
| | 28472 | 2·807 | | 25950 | 3·824 | | 34560 | 3·384 |
| 187°·75 (Critical) | 24430 | 6·954 | | 26040 | 3·603 | | 36370 | 3·162 |
| | 24550 | 6·731 | | 26300 | 3·382 | | 37760 | 3·052 |
| | 24640 | 6·508 | | 26940 | 3·160 | | 39660 | 2·941 |
| | 24750 | 6·282 | | 28560 | 2·939 | | 42360 | 2·831 |
| | 24820 | 6·057 | | 30170 | 2·829 | | 46260 | 2·720 |
| | 24880 | 5·832 | | 32780 | 2·718 | | 52090 | 2·610 |
| | 24940 | 5·608 | | 36810 | 2·608 | 210° … | 29350 | 6·958 |
| | 24970 | 5·384 | | 43080 | 2·497 | | 30000 | 6·511 |
| | 25000 | 5·160 | | 53320 | 2·387 | | 30660 | 6·061 |
| | 25010 | 4·938 | 195° … | 26050 | 6·955 | | 31340 | 5·611 |
| | 25020 | 4·716 | | 26410 | 6·509 | | 32030 | 5·163 |
| | 25030 | 4·268 | | 26740 | 6·059 | | 32840 | 4·718 |
| | 25030 | 3·824 | | 27050 | 5·609 | | 33730 | 4·271 |
| 187°·8 (Critical) | 25040 | 3·603 | | 27320 | 5·161 | | 35040 | 3·826 |
| | 25110 | 3·382 | | 27560 | 4·717 | | 36010 | 3·605 |
| | 25610 | 3·160 | | 27810 | 4·270 | | 37410 | 3·384 |
| | 26140 | 3·050 | | 28150 | 3·825 | | 39580 | 3·162 |
| | 26970 | 2·939 | | 28450 | 3·604 | | 41210 | 3·052 |
| | 28430 | 2·829 | | 28980 | 3·383 | | 43500 | 2·941 |
| | 30790 | 2·718 | | 30000 | 3·161 | | 46580 | 2·831 |
| | 34570 | 2·608 | | 30880 | 3·051 | | 51040 | 2·720 |
| | 40670 | 2·497 | | 32220 | 2·940 | | 53910 | 2·660 |
| | 46050 | 2·431 | | 34200 | 2·830 | 220° … | 31480 | 6·959 |
| | 49580 | 2·394 | | 37150 | 2·719 | | 32330 | 6·513 |
| | 53680 | 2·361 | | 41770 | 2·609 | | 33260 | 6·062 |
| 188°·0 | 24910 | 6·057 | | 48930 | 2·498 | | 34170 | 5·612 |
| | 25010 | 5·608 | | 53150 | 2·449 | | 35180 | 5·164 |
| | 25070 | 5·160 | 200° … | 27180 | 6·956 | | 36330 | 4·719 |
| | 25090 | 4·716 | | 27630 | 6·510 | | 37730 | 4·272 |
| | 25100 | 4·492 | | 28080 | 6·059 | | 39720 | 3·827 |
| | 25100 | 4·268 | | 28520 | 5·609 | | 41080 | 3·606 |
| | 25110 | 4·046 | | 28890 | 5·161 | | 43100 | 3·385 |
| | 25130 | 3·824 | | 29310 | 4·717 | | 44460 | 3·274 |
| | 25160 | 3·603 | | 29750 | 4·270 | | 46150 | 3·163 |
| | 25300 | 3·382 | | 30410 | 3·825 | | 48450 | 3·053 |
| 188°·3 | 24940 | 6·057 | | 30930 | 3·604 | | 51170 | 2·942 |
| | 25070 | 5·608 | | 31740 | 3·383 | | 53960 | 2·857 |
| | 25140 | 5·160 | | 33150 | 3·161 | 230° … | 33610 | 6·961 |
| | 25170 | 4·938 | | 34310 | 3·051 | | 34650 | 6·515 |
| | 25180 | 4·716 | | 35910 | 2·940 | | 35750 | 6·064 |
| | 25190 | 4·492 | | 38220 | 2·830 | | 36940 | 5·614 |
| | 25190 | 4·268 | | 41710 | 2·719 | | 38260 | 5·165 |
| | 25210 | 4·046 | | 46900 | 2·609 | | 39800 | 4·720 |
| | 25220 | 3·824 | | 53160 | 2·516 | | 41750 | 4·273 |
| | 25250 | 3·603 | 205° … | 28290 | 6·957 | | 44440 | 3·828 |
| | 25400 | 3·382 | | 28820 | 6·510 | | 46360 | 3·607 |
| 190° … | 24920 | 6·954 | | 29390 | 6·060 | | 47640 | 3·496 |

## Series III. (*continued*).

| Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. |
|---|---|---|---|---|---|---|---|---|
| 230° ... | 49010 | 3·386 | 250° ... | 42550 | 5·616 | 270° ... | 41870 | 6·968 |
| (*cont.*) | 50780 | 3·275 | (*cont.*) | 44510 | 5·168 | | 43670 | 6·522 |
| | 52880 | 3·164 | | 46890 | 4·723 | | 45690 | 6·069 |
| 240° ... | 35700 | 6·963 | | 48350 | 4·500 | | 48030 | 5·619 |
| | 36950 | 6·516 | | 49910 | 4·275 | | 49320 | 5·395 |
| | 38310 | 6·065 | | 51900 | 4·053 | | 50700 | 5·170 |
| | 39750 | 5·615 | | 53000 | 3·940 | | 52230 | 4·948 |
| | 41440 | 5·167 | 260° ... | 39850 | 6·967 | | 53070 | 4·837 |
| | 43360 | 4·721 | | 41440 | 6·520 | 280° ... | 43890 | 6·970 |
| | 45930 | 4·274 | | 43240 | 6·068 | | 45940 | 6·523 |
| | 47490 | 4·052 | | 45280 | 5·618 | | 48240 | 6·071 |
| | 49370 | 3·829 | | 47590 | 5·169 | | 49410 | 5·846 |
| | 51780 | 3·608 | | 48920 | 4·947 | | 50770 | 5·621 |
| | 53320 | 3·497 | | 50430 | 4·724 | | 52170 | 5·396 |
| 250° ... | 37820 | 6·965 | | 52170 | 4·501 | | 52980 | 5·284 |
| | 39210 | 6·518 | | 53080 | 4·388 | | 53760 | 5·172 |
| | 40760 | 6·066 | | | | | | |

## SERIES IV.

| Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. |
|---|---|---|---|---|---|---|---|---|
| 150° ... | 12870 | 19·39 | 176° ... | 18230 | 13·15 | 183° ... | 23030 | 7·585 |
| | 13120 | 18·77 | (*cont.*) | 19090 | 11·91 | (*cont.*) | 23180 | 7·280 |
| | 13370 | 18·15 | | 19950 | 10·67 | | 23260 | 7·095 |
| | 13600 | 17·52 | | 20360 | 10·05 | 185° ... | 15020 | 19·41 |
| 160° ... | 13520 | 19·40 | | 20750 | 9·435 | | 15720 | 18·16 |
| | 14080 | 18·15 | | 20920 | 9·130 | | 16480 | 16·91 |
| | 14670 | 16·89 | 180° ... | 14730 | 19·41 | | 17300 | 15·65 |
| | 14980 | 16·27 | | 15400 | 18·16 | | 18190 | 14·40 |
| | 15290 | 15·64 | | 16130 | 16·90 | | 19130 | 13·16 |
| | 15610 | 15·02 | | 16910 | 15·65 | | 20110 | 11·91 |
| | 15940 | 14·39 | | 17750 | 14·40 | | 21130 | 10·67 |
| | 16260 | 13·77 | | 18620 | 13·15 | | 22150 | 9·440 |
| 170° ... | 14130 | 19·40 | | 19540 | 11·91 | | 23070 | 8·205 |
| | 14740 | 18·15 | | 20470 | 10·67 | | 23460 | 7·585 |
| | 15380 | 16·89 | | 21360 | 9·440 | | 23780 | 6·970 |
| | 16110 | 15·64 | | 21770 | 8·820 | | 23910 | 6·665 |
| | 16850 | 14·39 | | 22130 | 8·200 | | 24000 | 6·355 |
| | 17240 | 13·77 | | 22260 | 7·955 | 186° ... | 21260 | 10·67 |
| | 17620 | 13·16 | 183° ... | 14900 | 19·41 | | 22290 | 9·440 |
| | 18020 | 12·53 | | 15590 | 18·16 | | 23270 | 8·205 |
| | 18400 | 11·91 | | 16330 | 16·90 | | 23670 | 7·585 |
| | 18770 | 11·29 | | 17140 | 15·65 | | 24010 | 6·970 |
| | 18940 | 10·98 | | 18000 | 14·40 | | 24150 | 6·665 |
| 176° ... | 14480 | 19·41 | | 18920 | 13·16 | | 24270 | 6·355 |
| | 15130 | 18·15 | | 19880 | 11·91 | | 24350 | 6·045 |
| | 15840 | 16·90 | | 20870 | 10·67 | 187°·85 | 15190 | 19·41 |
| | 16600 | 15·64 | | 21820 | 9·440 | (Critical) | 15900 | 18·17 |
| | 17380 | 14·39 | | 22680 | 8·205 | | 16680 | 16·91 |

## Series IV. (*continued*).

| Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. |
|---|---|---|---|---|---|---|---|---|
| 187°·85 (Critical) (*cont.*) | 17510 | 15·65 | 210° ... (*cont.*) | 17310 | 18·17 | 250° ... | 18760 | 19·44 |
| | 18430 | 14·40 | | 18220 | 16·92 | | 19780 | 18·19 |
| | 19390 | 13·16 | | 19220 | 15·66 | | 20920 | 16·94 |
| | 20400 | 11·91 | | 20300 | 14·41 | | 22170 | 15·68 |
| | 21480 | 10·67 | | 21500 | 13·17 | | 23600 | 14·43 |
| | 22560 | 9·440 | | 22820 | 11·92 | | 25190 | 13·18 |
| | 23570 | 8·205 | | 24280 | 10·68 | | 27010 | 11·93 |
| | 24430 | 6·970 | | 25840 | 9·445 | | 29130 | 10·69 |
| | 24910 | 5·740 | | 27520 | 8·210 | | 31520 | 9·455 |
| | 25000 | 5·125 | | 29300 | 6·975 | | 34340 | 8·220 |
| | 25020 | 4·505 | | 31150 | 5·740 | | 37740 | 6·980 |
| | 25030 | 3·890 | | 33260 | 4·505 | | 42030 | 5·750 |
| 190° ... | 15310 | 19·41 | 220° ... | 17060 | 19·43 | | 44630 | 5·130 |
| | 16040 | 18·17 | | 17930 | 18·18 | 260° ... | 19320 | 19·45 |
| | 16840 | 16·91 | | 18900 | 16·93 | | 20360 | 18·20 |
| | 17690 | 15·65 | | 19960 | 15·66 | | 21570 | 16·94 |
| | 18600 | 14·40 | | 21150 | 14·41 | | 22910 | 15·68 |
| | 19590 | 13·16 | | 22430 | 13·17 | | 24410 | 14·43 |
| | 20640 | 11·91 | | 23870 | 11·92 | | 26100 | 13·18 |
| | 21750 | 10·67 | | 25500 | 10·68 | | 28050 | 11·94 |
| | 22880 | 9·440 | | 27270 | 9·450 | | 30300 | 10·70 |
| | 23940 | 8·205 | | 29250 | 8·210 | | 32920 | 9·460 |
| | 24900 | 6·970 | | 31440 | 6·975 | | 36050 | 8·220 |
| | 25540 | 5·740 | | 33860 | 5·745 | | 39780 | 6·980 |
| | 25820 | 4·505 | | 36930 | 4·510 | | 44640 | 5·750 |
| 195° ... | 15610 | 19·42 | 230° ... | 17630 | 19·43 | | 47840 | 5·135 |
| | 16370 | 18·16 | | 18540 | 18·18 | 270° ... | 19880 | 19·45 |
| | 17180 | 16·91 | | 19560 | 16·93 | | 20980 | 18·20 |
| | 18070 | 15·65 | | 20690 | 15·67 | | 22230 | 16·95 |
| | 19030 | 14·40 | | 21940 | 14·42 | | 23610 | 15·69 |
| | 20080 | 13·16 | | 23350 | 13·17 | | 24200 | 14·44 |
| | 21200 | 11·91 | | 24930 | 11·93 | | 27000 | 13·19 |
| | 22400 | 10·67 | | 26690 | 10·69 | | 29080 | 11·94 |
| | 23630 | 9·440 | | 28690 | 9·450 | | 31460 | 10·70 |
| | 24880 | 8·205 | | 30940 | 8·215 | | 34280 | 9·460 |
| | 26020 | 6·970 | | 33550 | 6·975 | | 37690 | 8·225 |
| | 26980 | 5·740 | | 36570 | 5·745 | | 41820 | 6·985 |
| | 27650 | 4·505 | | 40630 | 4·510 | | 47390 | 5·755 |
| 200° ... | 15910 | 19·42 | 240° ... | 18210 | 19·44 | | 50900 | 5·135 |
| | 16680 | 18·17 | | 19170 | 18·19 | 280° ... | 20410 | 19·46 |
| | 17530 | 16·92 | | 20250 | 16·94 | | 21570 | 18·21 |
| | 18450 | 15·65 | | 21450 | 15·67 | | 22870 | 16·95 |
| | 19470 | 14·41 | | 22780 | 14·42 | | 24340 | 15·69 |
| | 20560 | 13·16 | | 24300 | 13·18 | | 26000 | 14·44 |
| | 21740 | 11·92 | | 25980 | 11·93 | | 27890 | 13·19 |
| | 23030 | 10·68 | | 27960 | 10·69 | | 30070 | 11·94 |
| | 24380 | 9·445 | | 30120 | 9·455 | | 32600 | 10·70 |
| | 25790 | 8·205 | | 32690 | 8·215 | | 35630 | 9·465 |
| | 27140 | 6·970 | | 35700 | 6·980 | | 39280 | 8·225 |
| | 28390 | 5·740 | | 39310 | 5·745 | | 43810 | 6·985 |
| | 29500 | 4·505 | | 41540 | 5·130 | | 49930 | 5·755 |
| 210° ... | 16490 | 19·42 | | | | | | |

## SERIES V.

| Temp. | Pressure. millim | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. |
|---|---|---|---|---|---|---|---|---|
| 140° ... | 11160 | 22·63 | 180° ... | 19940 | 11·37 | 240° ... | 23850 | 13·49 |
|  | 11375 | 21·93 | (*cont*) | 20470 | 10·67 | (*cont.*) | 25750 | 12·09 |
|  | 11490 | 21·58 |  | 20970 | 9·980 |  | 27890 | 10·69 |
|  | 11595 | 21·22 |  | 21470 | 9·280 |  | 30390 | 9·290 |
| 150° ... | 11920 | 21·93 |  | 21900 | 8·580 |  | 31820 | 8·590 |
|  | 12170 | 21·23 |  | 22100 | 8·235 |  | 33370 | 7·895 |
|  | 12430 | 20·52 | 200° ... | 14510 | 21·96 |  | 35090 | 7·200 |
|  | 12700 | 19·81 |  | 15640 | 19·84 |  | 36940 | 6·500 |
|  | 12970 | 19·10 |  | 16970 | 17·71 |  | 39100 | 5·805 |
|  | 13260 | 18·39 |  | 18500 | 15·59 |  | 41680 | 5·105 |
|  | 13550 | 17·69 |  | 20260 | 13·48 |  | 45050 | 4·410 |
|  | 13700 | 17·30 |  | 21570 | 12·08 | 260° ... | 17440 | 21·99 |
| 160°... | 12470 | 21·94 |  | 23010 | 10·68 |  | 18960 | 19·87 |
|  | 13030 | 20·53 |  | 24550 | 9·280 |  | 20780 | 17·74 |
|  | 13600 | 19·11 |  | 25310 | 8·585 |  | 22960 | 15·62 |
|  | 14290 | 17·69 |  | 26100 | 7·890 |  | 25610 | 13·50 |
|  | 14620 | 16·98 |  | 26890 | 7·190 |  | 27750 | 12·10 |
|  | 14970 | 16·28 |  | 27620 | 6·495 |  | 30260 | 10·70 |
|  | 15330 | 15·58 |  | 28320 | 5·800 |  | 33240 | 9·295 |
|  | 15680 | 14·88 |  | 28970 | 5·100 |  | 34950 | 8·595 |
|  | 16050 | 14·17 |  | 29590 | 4·405 |  | 36850 | 7·900 |
| 170° ... | 12990 | 21·94 | 220° ... | 15500 | 21·97 |  | 39020 | 7·205 |
|  | 13600 | 20·53 |  | 16760 | 19·85 |  | 41400 | 6·505 |
|  | 14260 | 19·11 |  | 18250 | 17·72 |  | 44270 | 5·805 |
|  | 14960 | 17·70 |  | 19990 | 15·60 |  | 47940 | 5·110 |
|  | 15740 | 16·28 |  | 22080 | 13·49 |  | 52780 | 4·410 |
|  | 16560 | 14·88 |  | 23660 | 12·08 | 280° ... | 18390 | 22·01 |
|  | 17410 | 13·47 |  | 25450 | 10·69 |  | 20030 | 19·88 |
|  | 17850 | 12·77 |  | 27480 | 9·285 |  | 22000 | 17·75 |
|  | 18290 | 12·07 |  | 28580 | 8·590 |  | 24390 | 15·63 |
|  | 18710 | 11·37 |  | 29770 | 7·890 |  | 27350 | 13·51 |
|  | 18930 | 11·02 |  | 31010 | 7·195 |  | 29740 | 12·11 |
| 180° ... | 13500 | 21·95 |  | 32320 | 6·500 |  | 32600 | 10·71 |
|  | 14150 | 20·54 |  | 33710 | 5·800 |  | 36030 | 9·300 |
|  | 14860 | 19·12 |  | 35310 | 5·100 |  | 38060 | 8·600 |
|  | 15640 | 17·70 |  | 37240 | 4·405 |  | 40260 | 7·905 |
|  | 16490 | 16·29 | 240° ... | 16470 | 21·98 |  | 42890 | 7·210 |
|  | 17400 | 14·88 |  | 17870 | 19·86 |  | 45920 | 6·510 |
|  | 18390 | 13·47 |  | 19530 | 17·73 |  | 49530 | 5·810 |
|  | 19420 | 12·07 |  | 21480 | 15·61 |  |  |  |

## SERIES VI.

| Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. |
|---|---|---|---|---|---|---|---|---|
| 90° ... | 3585 | 76·62 | 140° ... | 9411 | 29·06 | 180° ... | 12500 | 24·37 |
| | 3678 | 74·24 | *(cont.)* | 9993 | 26·69 | *(cont.)* | 13480 | 22·01 |
| | 3786 | 71·86 | | 10640 | 24·34 | | 14580 | 19·64 |
| | 3895 | 69·47 | | 11360 | 21·98 | | 15890 | 17·28 |
| | 4012 | 67·07 | 150° ... | 4463 | 74·35 | | 17380 | 14·91 |
| | 4135 | 64·67 | | 4887 | 67·17 | | 19070 | 12·56 |
| | 4263 | 62·26 | | 5400 | 59·96 | 200° ... | 5084 | 74·45 |
| 100° ... | 3813 | 74·26 | | 6037 | 52·79 | | 5577 | 67·26 |
| | 4040 | 69·49 | | 6830 | 45·63 | | 6186 | 60·04 |
| | 4297 | 64·68 | | 7498 | 40·89 | | 6943 | 52·86 |
| | 4432 | 62·28 | | 8267 | 36·17 | | 7893 | 45·70 |
| | 4585 | 59·88 | | 9198 | 31·43 | | 8697 | 40·94 |
| | 4739 | 57·49 | | 10410 | 26·70 | | 9672 | 36·21 |
| | 4910 | 55·10 | | 11110 | 24·34 | | 10890 | 31·47 |
| | 5081 | 52·73 | | 11900 | 21·98 | | 12430 | 26·74 |
| | 5271 | 50·35 | | 12770 | 19·63 | | 13370 | 24·38 |
| 110° ... | 3946 | 74·27 | | 13740 | 17·26 | | 14460 | 22·02 |
| | 4182 | 69·51 | 160° ... | 4589 | 74·37 | | 15740 | 19·65 |
| | 4447 | 64·70 | | 5032 | 67·19 | | 17250 | 17·29 |
| | 4749 | 59·90 | | 5564 | 59·98 | | 19010 | 14·92 |
| | 5091 | 55·11 | | 6224 | 52·81 | 220° ... | 5317 | 74·48 |
| | 5482 | 50·37 | | 7056 | 45·64 | | 5847 | 67·30 |
| | 5933 | 45·59 | | 7734 | 40·90 | | 6491 | 60·07 |
| | 6185 | 43·22 | | 8564 | 36·18 | | 7294 | 52·89 |
| | 6472 | 40·85 | | 9573 | 31·44 | | 8314 | 45·72 |
| 120° ... | 4079 | 74·29 | | 10840 | 26·71 | | 9182 | 40·96 |
| | 4458 | 67·12 | | 12430 | 21·99 | | 10220 | 36·23 |
| | 4918 | 59·91 | | 13400 | 19·63 | | 11530 | 31·49 |
| | 5472 | 52·75 | | 14480 | 17·26 | | 13210 | 26·75 |
| | 6167 | 45·60 | | 15660 | 14·90 | | 14250 | 24·39 |
| | 6717 | 40·86 | 170° ... | 4713 | 74·39 | | 15450 | 22·03 |
| | 7040 | 38·50 | | 5172 | 67·21 | | 16880 | 19·66 |
| | 7376 | 36·14 | | 5724 | 59·99 | | 18580 | 17·30 |
| | 7754 | 33·76 | | 6403 | 52·82 | | 20620 | 14·93 |
| | 7958 | 32·59 | | 7272 | 45·66 | 240° ... | 5562 | 74·52 |
| 130° ... | 4206 | 74·31 | | 7979 | 40·91 | | 6119 | 67·34 |
| | 4603 | 67·14 | | 8844 | 36·19 | | 6807 | 60·10 |
| | 5079 | 59·93 | | 9910 | 31·45 | | 7657 | 52·92 |
| | 5665 | 52·76 | | 11250 | 26·71 | | 8740 | 45·74 |
| | 6396 | 45·61 | | 12050 | 24·36 | | 9658 | 40·98 |
| | 6985 | 40·87 | | 12960 | 22·00 | | 10780 | 36·25 |
| | 7689 | 36·15 | | 14010 | 19·64 | | 12180 | 31·50 |
| | 8083 | 33·77 | | 15200 | 17·27 | | 14010 | 26·76 |
| | 8527 | 31·41 | | 16540 | 14·90 | | 15120 | 24·40 |
| | 9012 | 29·05 | | 18000 | 12·55 | | 16440 | 22·04 |
| | 9553 | 26·69 | 180° ... | 4834 | 74·41 | | 18010 | 19·67 |
| 140° ... | 4337 | 74·33 | | 5302 | 67·22 | | 19910 | 17·30 |
| | 4751 | 67·16 | | 5876 | 60·01 | | 22230 | 14·94 |
| | 5242 | 59·95 | | 6583 | 52·83 | 260° ... | 5805 | 74·56 |
| | 5856 | 52·78 | | 7484 | 45·67 | | 6389 | 67·37 |
| | 6617 | 45·62 | | 8222 | 40·92 | | 7125 | 60·13 |
| | 7243 | 40·88 | | 9122 | 36·20 | | 8022 | 52·94 |
| | 7977 | 36·16 | | 10240 | 31·46 | | 9160 | 45·76 |
| | 8884 | 31·42 | | 11650 | 26·72 | | 10140 | 41·00 |

## Series VI. (*continued*).

| Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. |
|---|---|---|---|---|---|---|---|---|
| 260° ... | 11330 | 36·26 | 280° ... | 6675 | 67·40 | 280° ... | 18410 | 22·06 |
| (*cont.*) | 12830 | 31·52 | (*cont.*) | 7453 | 60·16 | (*cont.*) | 20250 | 19·69 |
|  | 14780 | 26·77 |  | 8380 | 52·97 |  | 22520 | 17·32 |
|  | 16000 | 24·41 |  | 9608 | 45·79 |  | 25330 | 14·95 |
|  | 17430 | 22·05 |  | 10660 | 41·03 |  | 27040 | 13·76 |
|  | 19130 | 19·68 |  | 11900 | 36·28 |  | 28980 | 12·59 |
|  | 21220 | 17·31 |  | 13490 | 31·53 |  | 31240 | 11·40 |
|  | 23760 | 14·94 |  | 15580 | 26·79 |  | 34870 | 10·21 |
| 280° ... | 6065 | 74·60 |  | 16870 | 24·43 |  | 37030 | 9·02 |

## SERIES VII.

| Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. |
|---|---|---|---|---|---|---|---|---|
| 50° ... | 1427 | 181·60 | 90° ... | 2054 | 142·05 | 120° ... | 3590 | 85·72 |
|  | 1471 | 175·95 | (*cont.*) | 2311 | 125·05 | (*cont.*) | 4065 | 74·50 |
|  | 1514 | 170·30 |  | 2639 | 108·10 |  | 4687 | 63·30 |
| 60° ... | 1479 | 181·65 |  | 2913 | 96·86 |  | 5530 | 52·13 |
|  | 1524 | 176·00 |  | 3252 | 85·66 | 130° ... | 1886 | 176·30 |
|  | 1570 | 170·35 |  | 3448 | 80·04 |  | 2076 | 159·25 |
|  | 1620 | 164·70 |  | 3669 | 74·44 |  | 2313 | 142·20 |
|  | 1676 | 159·00 |  | 3923 | 68·85 |  | 2608 | 125·20 |
|  | 1732 | 153·30 |  | 4209 | 63·25 |  | 2984 | 108·20 |
|  | 1793 | 147·60 | 100° ... | 1732 | 176·15 |  | 3303 | 96·96 |
|  | 1858 | 141·90 |  | 1906 | 159·15 |  | 3698 | 85·75 |
|  | 1927 | 136·25 |  | 2120 | 142·10 |  | 4193 | 74·52 |
|  | 2001 | 130·60 |  | 2388 | 125·10 |  | 4841 | 63·32 |
| 70° ... | 1575 | 176·05 |  | 2727 | 108·15 |  | 5717 | 52·14 |
|  | 1679 | 164·70 |  | 3012 | 96·88 | 140° ... | 1936 | 176·35 |
|  | 1793 | 153·30 |  | 3360 | 85·68 |  | 2133 | 159·30 |
|  | 1924 | 141·90 |  | 3803 | 74·46 |  | 2377 | 142·25 |
|  | 2077 | 130·60 |  | 4368 | 63·27 |  | 2681 | 125·25 |
|  | 2253 | 119·35 |  | 5126 | 52·10 |  | 3071 | 108·25 |
|  | 2354 | 113·70 | 110° ... | 1784 | 176·20 |  | 3401 | 96·98 |
|  | 2462 | 108·05 |  | 1963 | 159·20 |  | 3808 | 85·78 |
|  | 2583 | 102·45 |  | 2185 | 142·10 |  | 4326 | 74·54 |
| 80° ... | 1627 | 176·10 |  | 2461 | 125·10 |  | 5000 | 63·34 |
|  | 1731 | 164·75 |  | 2816 | 108·15 |  | 5914 | 52·16 |
|  | 1851 | 153·35 |  | 3113 | 96·91 | 160° ... | 2035 | 176·45 |
|  | 1986 | 141·95 |  | 3474 | 85·70 |  | 2242 | 159·40 |
|  | 2146 | 130·65 |  | 3943 | 74·48 |  | 2503 | 142·35 |
|  | 2332 | 119·40 |  | 4534 | 63·29 |  | 2824 | 125·35 |
|  | 2552 | 108·05 |  | 5328 | 52·11 |  | 3238 | 108·30 |
|  | 2813 | 96·83 | 120° ... | 1837 | 176·25 |  | 3591 | 97·03 |
|  | 2965 | 91·24 |  | 2020 | 159·20 |  | 4023 | 85·82 |
|  | 3134 | 85·64 |  | 2251 | 142·15 |  | 4577 | 74·58 |
|  | 3321 | 79·99 |  | 2537 | 125·15 |  | 5296 | 63·37 |
| 90° ... | 1681 | 176·10 |  | 2902 | 108·20 |  | 6292 | 52·18 |
|  | 1848 | 159·10 |  | 3209 | 96·93 |  |  |  |

## Series VII. (*continued*).

| Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. |
|---|---|---|---|---|---|---|---|---|
| 180° ... | 2132 | 176·55 | 200° .. | 5888 | 63·43 | 250° ... | 4979 | 86·01 |
| | 2353 | 159·50 | (*cont.*) | 7025 | 52·23 | (*cont.*) | 5679 | 74·76 |
| | 2625 | 142·35 | 220° ... | 2330 | 176·75 | | 6620 | 63·51 |
| | 2966 | 125·35 | | 2575 | 159·70 | | 7211 | 57·92 |
| | 3405 | 108·35 | | 2877 | 142·50 | | 7910 | 52·30 |
| | 3775 | 97·08 | | 3253 | 125·50 | | 8781 | 46·68 |
| | 4239 | 85·86 | | 3738 | 108·45 | | 9871 | 41·06 |
| | 4822 | 74·62 | | 4156 | 97·18 | | 11275 | 35·44 |
| | 5590 | 63·40 | | 4666 | 85·95 | 280° ... | 2622 | 177·00 |
| | 6654 | 52·20 | | 5318 | 74·70 | | 2912 | 159·90 |
| 200° ... | 2231 | 176·65 | | 6176 | 63·46 | | 3252 | 142·75 |
| | 2463 | 159·60 | | 7381 | 52·26 | | 3680 | 125·70 |
| | 2751 | 142·45 | 250° ... | 2477 | 176·90 | | 4234 | 108·65 |
| | 3108 | 125·45 | | 2741 | 159·80 | | 4712 | 97·33 |
| | 3571 | 108·40 | | 3068 | 142·60 | | 5303 | 86·08 |
| | 3962 | 97·13 | | 3469 | 125·60 | | 6043 | 74·81 |
| | 4452 | 85·90 | | 3984 | 108·55 | | 7065 | 63·56 |
| | 5066 | 74·66 | | 4431 | 97·26 | | 8459 | 52·34 |

## SERIES VIII.

| Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. |
|---|---|---|---|---|---|---|---|---|
| 30° ... | 776 | 321·2 | 60° .. | 1857 | 141·9 | 90° ... | 1152 | 261·7 |
| | 797 | 312·6 | (*cont.*) | 1964 | 133·4 | (*cont.*) | 1317 | 227·4 |
| | 816 | 304·0 | 70° ... | 825 | 347·4 | | 1418 | 210·3 |
| 40° ... | 786 | 329·9 | | 866 | 330·2 | | 1537 | 193·2 |
| | 827 | 312·7 | | 965 | 295·7 | | 1678 | 176·2 |
| | 873 | 295·5 | | 1085 | 261·6 | | 1846 | 159·1 |
| | 924 | 278·5 | | 1239 | 227·3 | | 2054 | 142·0 |
| | 980 | 261·4 | | 1334 | 210·2 | | 2314 | 124·9 |
| | 1044 | 244·2 | | 1444 | 193·1 | 100° ... | 822 | 382·2 |
| | 1117 | 227·1 | | 1574 | 176·1 | | 860 | 365·0 |
| 50° ... | 814 | 330·0 | | 1732 | 159·0 | | 947 | 330·4 |
| | 903 | 295·6 | | 1922 | 142·0 | | 1054 | 296·0 |
| | 1015 | 261·4 | | 2164 | 124·9 | | 1186 | 261·8 |
| | 1082 | 244·3 | 80° ... | 812 | 364·8 | | 1357 | 227·5 |
| | 1158 | 227·2 | | 893 | 330·2 | | 1462 | 210·4 |
| | 1246 | 210·1 | | 993 | 295·8 | | 1584 | 193·2 |
| | 1348 | 193·0 | | 1118 | 261·7 | | 1732 | 176·3 |
| | 1468 | 176·0 | | 1277 | 227·4 | | 1904 | 159·2 |
| 60° .. | 799 | 347·4 | | 1377 | 210·3 | | 2120 | 142·1 |
| | 839 | 330·1 | | 1492 | 193·2 | | 2389 | 124·9 |
| | 933 | 295·7 | | 1627 | 176·2 | 120° ... | 832 | 399·6 |
| | 1049 | 261·5 | | 1789 | 159·1 | | 909 | 365·2 |
| | 1199 | 227·3 | | 1988 | 142·0 | | 1002 | 330·5 |
| | 1290 | 210·2 | | 2236 | 124·9 | | 1113 | 296·1 |
| | 1397 | 193·1 | 90° ... | 835 | 364·9 | | 1254 | 261·9 |
| | 1524 | 176·1 | | 920 | 330·3 | | 1435 | 227·6 |
| | 1673 | 159·0 | | 1024 | 295·9 | | 1547 | 210·5 |

### Series VIII. (*continued*).

| Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. | Temp. | Pressure. millim. | Volume. cub. cm. |
|---|---|---|---|---|---|---|---|---|
| 120° ... | 1678 | 193·4 | 180° ... | 853 | 452·3 | 220° ... | 1820 | 228·2 |
| (*cont.*) | 1834 | 176·4 |  | 963 | 400·2 | (*cont.*) | 1963 | 211·0 |
|  | 2020 | 159 3 |  | 1051 | 365·7 |  | 2130 | 193·9 |
|  | 2248 | 142·1 |  | 1159 | 331·1 |  | 2332 | 176·8 |
|  | 2536 | 125·0 |  | 1290 | 296·6 |  | 2573 | 159·7 |
| 140° ... | 838 | 417·1 |  | 1455 | 262·4 | 250° ... | 854 | 523·0 |
|  | 956 | 365·4 |  | 1677 | 228·0 |  | 915 | 488·2 |
|  | 1053 | 330·7 |  | 1800 | 210·8 |  | 1025 | 435·8 |
|  | 1172 | 296·3 |  | 1951 | 193·7 |  | 1161 | 383·6 |
|  | 1321 | 262·1 |  | 2135 | 176·7 |  | 1340 | 331·6 |
|  | 1513 | 227·7 |  | 2358 | 159·5 |  | 1495 | 297·2 |
|  | 1632 | 210·6 |  | 2625 | 142·3 |  | 1686 | 262·8 |
|  | 1770 | 193·5 |  | 2970 | 125·2 |  | 1934 | 228·3 |
|  | 1933 | 176·5 | 200° ... | 857 | 470·1 |  | 2088 | 211·2 |
|  | 2133 | 159·3 |  | 964 | 417·8 |  | 2269 | 194·0 |
|  | 2377 | 142·2 |  | 1098 | 366·0 |  | 2480 | 177·0 |
|  | 2684 | 125·1 |  | 1209 | 331·2 |  | 2740 | 159·8 |
| 160° ... | 847 | 434·7 |  | 1349 | 296·8 | 280° ... | 876 | 540·8 |
|  | 958 | 382·8 |  | 1521 | 262·5 |  | 970 | 488·5 |
|  | 1107 | 330·9 |  | 1744 | 228·1 |  | 1084 | 436·1 |
|  | 1233 | 296·4 |  | 1880 | 211·0 |  | 1230 | 384·0 |
|  | 1388 | 262·2 |  | 2041 | 193·8 |  | 1420 | 331·9 |
|  | 1591 | 227·8 |  | 2233 | 176·7 |  | 1583 | 297·4 |
|  | 1716 | 210·7 |  | 2466 | 159·6 |  | 1786 | 263·0 |
|  | 1861 | 193·6 | 220° ... | 861 | 487·8 |  | 2049 | 228·5 |
|  | 2036 | 176·6 |  | 966 | 435·4 |  | 2213 | 211·4 |
|  | 2247 | 159·4 |  | 1093 | 383 4 |  | 2402 | 194·2 |
|  | 2503 | 142·3 |  | 1261 | 331·4 |  | 2631 | 177·1 |
|  | 2825 | 125·2 |  | 1407 | 297·0 |  | 2907 | 159·9 |
|  |  |  |  | 1587 | 262·6 |  |  |  |

### *The Critical Volume and Density.*

It is impossible to determine the critical volume accurately by direct experiment, but it may be calculated from the critical density, which may be ascertained with great accuracy by the method of Cailletet and Mathias (*Compt. Rend.* cii. p. 1202, civ. p. 1563; Mathias, *ibid.* cxv. p. 35).

In the following table the densities (mass of 1 cub. centim.) of liquid and saturated vapour and the mean densities are given at a series of temperatures, together with the mean densities calculated from the formula

$$D=0{\cdot}3197-0{\cdot}000454\,t.$$

The close agreement between the calculated and observed mean densities over such a wide range of temperature in this, as in so many other cases, justifies the very small extrapolation to the critical temperature. The mean density at this temperature, 187°·8, calculated from the formula, is 0·2344, and this is the critical density, for, at the critical temperature, the difference between the liquid and saturated vapour ceases to exist. The critical volume of a gram, calculated from the density, is 4·266 cub. centim.

Mean Densities of Liquid and Saturated Vapour.

| Temperature. | Density. | | | | |
|---|---|---|---|---|---|
| | Liquid. | Saturated Vapour. | Mean. | Calculated. | Δ × 10,000. |
| 10° | ·6295 | ·0016 | ·3156 | ·3152 | −4 |
| 20 | ·6196 | ·0024 | ·3110 | ·3106 | −4 |
| 30 | ·6092 | ·0033 | ·3062 | ·3061 | −1 |
| 40 | ·5988 | ·0045 | ·3017 | ·3015 | −2 |
| 50 | ·5881 | ·0060 | ·2970 | ·2970 | 0 |
| 60 | ·5769 | ·0078 | ·2924 | ·2924 | 0 |
| 70 | ·5656 | ·0101 | ·2878 | ·2879 | +1 |
| 80 | ·5540 | ·0128 | ·2834 | ·2834 | 0 |
| 90 | ·5413 | ·0162 | ·2787 | ·2788 | +1 |
| 100 | ·5278 | ·0203 | ·2741 | ·2743 | +2 |
| 110 | ·5140 | ·0251 | ·2695 | ·2697 | +2 |
| 120 | ·4991 | ·0311 | ·2651 | ·2652 | +1 |
| 130 | ·4826 | ·0383 | ·2605 | ·2607 | +2 |
| 140 | ·4642 | ·0473 | ·2557 | ·2561 | +4 |
| 150 | ·4445 | ·0583 | ·2514 | ·2516 | +2 |
| 160 | ·4206 | ·0729 | ·2468 | ·2470 | +2 |
| 170 | ·3914 | ·0932 | ·2423 | ·2425 | +2 |
| 176 | ·3694 | ·1103 | ·2398 | ·2398 | 0 |
| 180 | ·3498 | ·1258 | ·2378 | ·2380 | +2 |
| 183 | ·3311 | ·1422 | ·2366 | ·2366 | 0 |
| 185 | ·3142 | ·1575 | ·2358 | ·2357 | −1 |
| 186 | ·3028 | ·1677 | ·2353 | ·2352 | −1 |
| 187 | ·2857 | ·1834 | ·2346 | ·2348 | +2 |
| 187·4 | ·2761 | ·1951 | ·2356 | ·2346 | −10 |
| (Critical) 187°·8 | …… | …… | …… | ·2344 | |

| | |
|---|---|
| Critical Volume of a gram……… | 4·266 cub. cm. |
| Critical Molecular Volume……… | 306·5 cub. cm. |

## THEORETICAL CONCLUSIONS.

### *Relation of Pressure to Temperature at Constant Volume. Isochors.*

For the larger volumes of a gram the pressures corresponding to definite volumes were read from the isothermals constructed from the data already given. This method was, however, not practicable in the case of the smaller volumes. Isobars were therefore first constructed, and the temperatures at definite volumes were then read from the isobars. The data from which the isobars were constructed are given in the table below, p. 638.

In the tables which follow (pp. 639–643) the data for two sets of isochors are given, those at smaller volumes from the isobars and those at larger volumes from the isotherms. The pressures read from the isothermals constructed from the data obtained by Thomas and myself by the modified Hofmann's vapour-density method are included in the second set.

Isobars, read from Isothermals.

| Pressure in metres. | 4 | 8 | 12 | 16 | 20 | 24 | 28 | 32 | 36 | 40 | 44 | 48 | 52 | 56 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Temp. | Volume in cub. centims. | | | | | | | | | | | | | |
| 10° | 1·5871 | 1·5854 | 1·5838 | 1·5820 | 1·5806 | 1·5790 | 1·5773 | 1·5757 | 1·5742 | 1·5726 | 1·5711 | 1·5696 | 1·5682 | 1·5667 |
| 15·6 | 1·6012 | 1·5994 | 1·5976 | 1·5959 | 1·5941 | 1·5923 | 1·5906 | 1·5889 | 1·5872 | 1·5856 | 1·5839 | 1·5821 | 1·5806 | 1·5791 |
| 30 | 1·6388 | 1·6366 | 1·6344 | 1·6322 | 1·6300 | 1·6280 | 1·6260 | 1·6240 | 1·6220 | 1·6202 | 1·6184 | 1·6166 | 1·6149 | 1·6131 |
| 40 | 1·6681 | 1·6655 | 1·6630 | 1·6605 | 1·6581 | 1·6556 | 1·6533 | 1·6510 | 1·6487 | 1·6465 | 1·6444 | 1·6423 | 1·6402 | 1·6382 |
| 50 | 1·6984 | 1·6953 | 1·6924 | 1·6896 | 1·6868 | 1·6841 | 1·6814 | 1·6788 | 1·6763 | 1·6739 | 1·6715 | 1·6691 | 1·6668 | 1·6645 |
| 60 | 1·7312 | 1·7277 | 1·7244 | 1·7210 | 1·7179 | 1·7148 | 1·7116 | 1·7086 | 1·7057 | 1·7027 | 1·6999 | 1·6971 | 1·6944 | 1·6916 |
| 70 | 1·7666 | 1·7625 | 1·7585 | 1·7547 | 1·7510 | 1·7474 | 1·7440 | 1·7405 | 1·7372 | 1·7339 | 1·7306 | 1·7275 | 1·7244 | 1·7212 |
| 80 | 1·8038 | 1·7992 | 1·7948 | 1·7904 | 1·7861 | 1·7820 | 1·7780 | 1·7740 | 1·7700 | 1·7663 | 1·7625 | 1·7589 | 1·7552 | 1·7516 |
| 90 | 1·8477 | 1·8420 | 1·8364 | 1·8309 | 1·8255 | 1·8203 | 1·8154 | 1·8106 | 1·8060 | 1·8014 | 1·7974 | 1·7934 | 1·7893 | 1·7749 |
| 100 | ...... | 1·8896 | 1·8825 | 1·8760 | 1·8695 | 1·8634 | 1·8576 | 1·8516 | 1·8460 | 1·8406 | 1·8356 | 1·8306 | 1·8256 | 1·8008 |
| 110 | ...... | 1·9417 | 1·9334 | 1·9253 | 1·9176 | 1·9102 | 1·9029 | 1·8961 | 1·8895 | 1·8830 | 1·8771 | 1·8710 | 1·8652 | 1·8596 |
| 120 | ...... | 2·0037 | 1·9922 | 1·9815 | 1·9713 | 1·9615 | 1·9527 | 1·9445 | 1·9365 | 1·9287 | 1·9215 | 1·9150 | 1·9083 | 1·9015 |
| 130 | ...... | ...... | 2·0630 | 2·0485 | 2·0350 | 2·0230 | 2·0115 | 2·0005 | 1·9910 | 1·9810 | 1·9715 | 1·9630 | 1·9540 | 1·9463 |
| 140 | ...... | ...... | 2·1512 | 2·1290 | 2·1105 | 2·0940 | 2·0787 | 2·0650 | 2·0520 | 2·0405 | 2·0287 | 2·0185 | 2·0085 | 1·9987 |
| 150 | ...... | ...... | ...... | 2·2317 | 2·2035 | 2·1782 | 2·1565 | 2·1385 | 2·1210 | 2·1050 | 2·0912 | 2·0780 | 2·0655 | 2·0537 |
| 160 | ...... | ...... | ...... | ...... | 2·3285 | 2·2900 | 2·2575 | 2·2305 | 2·2062 | 2·1852 | 2·1657 | 2·1485 | 2·1322 | 2·1180 |
| 170 | ...... | ...... | ...... | ...... | 2·5252 | 2·4485 | 2·3882 | 2·3450 | 2·3080 | 2·2777 | 2·2512 | 2·2270 | 2·2057 | 2·1872 |
| 176 | ...... | ...... | ...... | ...... | ...... | 2·5800 | 2·4925 | 2·4315 | 2·3835 | 2·3440 | 2·3112 | 2·2837 | 2·2585 | 2·2362 |
| 180 | ...... | ...... | ...... | ...... | ...... | 2·7230 | 2·5835 | 2·5005 | 2·4405 | 2·3985 | 2·3550 | 2·3245 | ...... | ...... |
| 183 | ...... | ...... | ...... | ...... | ...... | 2·9050 | 2·6645 | 2·5590 | 2·4890 | 2·4335 | 2·3912 | 2·3550 | 2·3250 | 2·3000 |
| 185 | ...... | ...... | ...... | ...... | ...... | 3·1830 | 2·7345 | 2·6050 | 2·5270 | 2·4645 | 2·4165 | ...... | ...... | ...... |
| 186 | ...... | ...... | ...... | ...... | ...... | ...... | 2·7725 | ...... | ...... | ...... | ...... | ...... | ...... | ...... |
| 187·4 | ...... | ...... | ...... | ...... | ...... | ...... | 2·8360 | ...... | ...... | ...... | ...... | ...... | ...... | ...... |
| 187·8 | ...... | ...... | ...... | ...... | ...... | ...... | 2·8585 | 2·6770 | 2·5790 | 2·5075 | 2·4550 | 2·4115 | 2·3745 | 2·3445 |
| 190 | ...... | ...... | ...... | ...... | ...... | ...... | ...... | 2·7440 | 2·6260 | 2·5480 | 2·4880 | 2·4405 | 2·4000 | 2·3645 |
| 195 | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | 2·7580 | 2·6460 | 2·5700 | 2·5095 | 2·4610 | 2·4200 |
| 200 | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | 2·9355 | 2·7700 | 2·6650 | 2·5900 | 2·5305 | 2·4845 |
| 205 | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | 2·7790 | 2·6815 | 2·6110 | ...... |
| 210 | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | 2·9195 | 2·7930 | 2·6990 | 2·6200 |
| 220 | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | 2·9145 | 2·8045 |

Isochors, read from Isobars.

| Pressure in metres. | 4 | 8 | 12 | 16 | 20 | 24 | 28 | 32 | 36 | 40 | 44 | 48 | 52 | 56 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Volume. | Temperature. | | | | | | | | | | | | | |
| | ° | ° | ° | ° | ° | ° | ° | ° | ° | ° | ° | ° | ° | ° |
| 1·58 | ...... | ...... | ...... | ...... | 9·75 | 10·45 | 11·15 | 11·90 | 12·50 | 13·15 | 13·95 | 14·65 | 15·35 | 16·05 |
| 1·60 | 15·2 | 15·95 | 16·65 | 17·45 | 18·1 | 18·9 | 19·65 | 20·4 | 21·05 | 21·8 | 22·55 | 23·35 | 24·0 | 24·75 |
| 1·65 | 33·9 | 34·7 | 35·5 | 36·4 | 37·15 | 38·0 | 38·9 | 39·75 | 40·5 | 41·35 | 42·15 | 42·9 | 43·7 | 44·55 |
| 1·70 | 50·5 | 51·45 | 52·4 | 53·35 | 54·3 | 55·25 | 56·2 | 57·15 | 58·1 | 59·05 | 60·0 | 60·95 | 61·9 | 62·95 |
| 1·75 | 65·4 | 66·5 | 67·55 | 68·65 | 69·75 | 70·7 | 71·85 | 72·95 | 74·0 | 75·05 | 76·1 | 77·25 | 78·35 | 79·45 |
| 1·80 | 78·95 | 80·1 | 81·2 | 82·45 | 83·65 | 84·75 | 85·95 | 87·2 | 88·3 | 89·6 | 90·7 | 91·8 | 93·0 | 94·3 |
| 1·85 | ...... | 91·8 | 93·0 | 94·45 | 95·7 | 97·0 | 98·4 | 99·75 | 101·0 | 102·35 | 103·7 | 105·0 | 106·3 | 107·7 |
| 1·90 | ...... | 102·2 | 103·6 | 105·05 | 106·5 | 107·9 | 109·35 | 110·85 | 112·3 | 113·8 | 115·3 | 116·75 | 118·25 | 119·75 |
| 1·95 | ...... | 111·3 | 112·95 | 114·6 | 116·2 | 117·8 | 119·45 | 121·0 | 122·6 | 124·2 | 125·75 | 127·35 | 129·1 | 130·7 |
| 2·0 | ...... | 119·55 | 121·15 | 122·9 | 124·75 | 126·65 | 128·5 | 129·95 | 131·6 | 133·3 | 135·0 | 136·8 | 138·55 | 140·2 |
| 2·1 | ...... | ...... | 134·55 | 136·7 | 138·7 | 140·75 | 142·95 | 145·0 | 147·05 | 149·15 | 151·15 | 153·3 | 155·3 | 157·5 |
| 2·2 | ...... | ...... | ...... | 147·25 | 149·7 | 152·2 | 154·65 | 157·0 | 159·3 | 161·7 | 164·25 | 166·75 | 169·15 | 171·6 |
| 2·3 | ...... | ...... | ...... | 155·25 | 158·0 | 160·75 | 163·5 | 166·4 | 169·3 | 172·1 | 174·95 | 177·7 | 180·45 | 183·2 |
| 2·4 | ...... | ...... | ...... | ...... | 164·45 | 167·45 | 170·7 | 173·8 | 177·2 | 180·5 | 183·7 | 186·8 | 190·0 | 193·2 |
| 2·5 | ...... | ...... | ...... | ...... | 169·15 | 172·65 | 176·4 | 180·0 | 183·7 | 187·3 | 190·9 | 194·3 | 198·0 | 201·3 |
| 2·6 | ...... | ...... | ...... | ...... | 172·3 | 176·75 | 180·65 | 184·75 | 188·85 | 192·75 | 196·7 | 200·6 | 204·3 | 208·7 |
| 2·7 | ...... | ...... | ...... | ...... | ...... | 179·55 | 184·15 | 188·7 | 193·0 | 197·3 | 201·6 | 205·85 | 210·05 | 214·7 |
| 2·8 | ...... | ...... | ...... | ...... | ...... | 181·55 | 186·7 | 191·4 | 196·3 | 201·0 | 205·75 | 210·25 | 215·0 | 219·75 |

## Isochors, read from Isothermals.

| Vol.... | 2·4 | 2·5 | 2·6 | 2·7 | 2·8 | 2·9 | 3·0 | 3·2 | 3·4 | 3·6 | 3·8 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Temp. | Pressures. | | | | | | | | | | |
| 170° | 27060 | 21020 | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 176 | 34520 | 27580 | 23360 | 21060 | ... | ... | ... | ... | ... | ... | ... |
| 180 | 39400 | 32060 | 27380 | 24460 | 22830 | ... | ... | ... | ... | ... | ... |
| 183 | 43120 | 35280 | 30260 | 27050 | 25130 | 24010 | 23360 | ... | ... | ... | ... |
| 185 | 45680 | 37480 | 32280 | 28850 | 26710 | 25420 | 24660 | ... | ... | ... | ... |
| 187·8 | 49080 | 40560 | 34980 | 31270 | 28940 | 27420 | 26460 | 25490 | 25130 | 25050 | 25030 |
| 190·0 | 52000 | 43140 | 37280 | 33270 | 30730 | 29070 | 27860 | 26770 | 26270 | 26070 | 25960 |
| 195 | ... | 48820 | 42320 | 37860 | 34880 | 32850 | 31460 | 29780 | 28940 | 28460 | 28190 |
| 200 | ... | 54560 | 47480 | 42490 | 39100 | 36680 | 35010 | 32870 | 31660 | 30950 | 30480 |
| 205 | ... | ... | ... | 47140 | 43270 | 40560 | 38550 | 35990 | 34430 | 33510 | 32820 |
| 210 | ... | ... | ... | 51990 | 47700 | 44510 | 42160 | 39090 | 37260 | 36020 | 35140 |
| 220 | ... | ... | ... | ... | ... | 52430 | 49630 | 45570 | 42940 | 41170 | 39910 |
| 230 | ... | ... | ... | ... | ... | ... | ... | 52100 | 48860 | 46460 | 44680 |
| 240 | ... | ... | ... | ... | ... | ... | ... | ... | .. | 51890 | 49690 |

## Isochors, read from Isothermals.

| Vol.... | 4·0 | Approx. Crit. 4·3 | 4·6 | 5·0 | 5·5 | 6·0 | 6·5 | 7·0 | 7·5 | 8·0 | 8·5 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Temp. | Pressures. | | | | | | | | | | |
| 180° | ... | ... | ... | ... | ... | ... | ... | ... | ... | 22230 | 21950 |
| 183 | ... | ... | ... | ... | ... | ... | ... | ... | 23090 | 22800 | 22490 |
| 185 | ... | ... | ... | ... | ... | ... | 23960 | 23770 | 23510 | 23200 | 22860 |
| 187·8 | 25020 | 25010 | 25000 | 24990 | 24940 | 24840 | 24660 | 24400 | 24070 | 23710 | 23330 |
| 190·0 | 25910 | 25860 | 25810 | 25760 | 25620 | 25420 | 25180 | 24880 | 24530 | 24110 | 23700 |
| 195 | 28000 | 27780 | 27650 | 27430 | 27130 | 26790 | 26420 | 26010 | 25570 | 25080 | 24590 |
| 200 | 30140 | 29730 | 29430 | 29060 | 28610 | 28150 | 27630 | 27100 | 26570 | 26010 | 25430 |
| 205 | 32310 | 31730 | 31260 | 30740 | 30070 | 29460 | 28840 | 28220 | ... | ... | ... |
| 210 | 34460 | 33680 | 33070 | 32350 | 31540 | 30760 | 30010 | 29280 | 28530 | 27820 | 27110 |
| 220 | 38890 | 37640 | 36640 | 35580 | 34420 | 33350 | 32340 | 31380 | 30460 | 29600 | 28750 |
| 230 | 43280 | 41590 | 40280 | 38850 | 37290 | 35920 | 34680 | 33500 | 32400 | 31370 | 30400 |
| 240 | 47900 | 45770 | 44010 | 42130 | 40170 | 38500 | 37000 | 35610 | 34330 | 33140 | 32030 |
| 250 | 52360 | 49770 | 47740 | 45440 | 43030 | 41020 | 39270 | 37680 | 36240 | 34900 | 33660 |
| 260 | ... | 53800 | 51380 | 48680 | 45890 | 43530 | 41480 | 39690 | 38080 | 36600 | 35220 |
| 270 | ... | ... | ... | 51910 | 48750 | 46070 | 43780 | 41770 | 39980 | 38360 | 36860 |
| 280 | ... | ... | ... | ... | 51540 | 48580 | 46000 | 43750 | 41770 | 40000 | 38380 |

## Isochors, read from Isothermals.

| Vol. ... | 9·0 | 9·5 | 10·0 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Temp. | Pressures. | | | | | | | | | | |
| 150° | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 13430 |
| 160 | ... | ... | ... | ... | ... | ... | 16160 | 15620 | 15110 | 14620 | 14140 |
| 170 | ... | ... | ... | 18950 | 18330 | 17710 | 17080 | 16490 | 15900 | 15330 | 14815 |
| 176 | ... | 20700 | 20390 | 19720 | 19020 | 18330 | 18630 | 17000 | 16370 | 15780 | 15210 |
| 180 | 21630 | 21300 | 20950 | 20210 | 19470 | 18730 | 18010 | 17320 | 16670 | 16040 | 15470 |
| 183 | 22130 | 21770 | 21380 | 20590 | 19800 | 19030 | 18280 | 17570 | 16920 | 16270 | 15680 |
| 185 | 22490 | 22090 | 21690 | 20870 | 20040 | 19250 | 18480 | 17750 | 17060 | 16420 | 15810 |
| 187·8 | 22930 | 22500 | 22040 | 21160 | 20300 | 19500 | 18720 | 17980 | 17260 | 16600 | 15990 |
| 190·0 | 23250 | 22820 | 22360 | 21440 | 20560 | 19710 | 18910 | 18150 | 17440 | 16780 | 16130 |
| 195 | 24080 | 23570 | 23060 | 22060 | 21100 | 20200 | 19350 | 18550 | 17810 | 17110 | 16470 |
| 200 | 24870 | 24310 | 23760 | 22680 | 21670 | 20710 | 19810 | 18970 | 18180 | 17460 | 16800 |
| 210 | 26430 | 25770 | 25110 | 23880 | 22720 | 21670 | 20670 | 19780 | 18930 | 18140 | 17430 |
| 220 | 27950 | 27170 | 26430 | 25050 | 23770 | 22620 | 21560 | 20570 | 19650 | 18830 | 18050 |
| 230 | 29480 | 28600 | 27750 | 26200 | 24830 | 23550 | 22400 | 21350 | 20370 | 19500 | 18690 |
| 240 | 30990 | 30010 | 29090 | 27400 | 25890 | 24500 | 23250 | 22130 | 21110 | 20180 | 19330 |
| 250 | 32510 | 31430 | 30410 | 28570 | 26900 | 25460 | 24120 | 22940 | 21840 | 20850 | 19940 |
| 260 | 33970 | 32790 | 31690 | 29700 | 27940 | 26370 | 24970 | 23700 | 22560 | 21510 | 20540 |
| 270 | 35460 | 34180 | 33000 | 30870 | 28980 | 27300 | 25810 | 24480 | 23260 | 22160 | 21150 |
| 280 | 36920 | 35530 | 34240 | 31950 | 29970 | 28190 | 26620 | 25220 | 23970 | 22810 | 21770 |

## Isochors, read from Isothermals.

| Vol. ... | 19 | 20 | 22 | 24 | 26 | 28 | 30 | 33 | 36 | 40 | 45 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Temp. | Pressures. | | | | | | | | | | |
| 110° | ... | ... | ... | .. | ... | ... | ... | ... | ... | 6570 | 5995 |
| 120 | ... | ... | ... | ... | ... | ... | ... | 7890 | 7400 | 6830 | 6235 |
| 130 | ... | ... | ... | ... | ... | 9250 | 8825 | 8220 | 7705 | 7100 | 6465 |
| 140 | ... | ... | 11355 | 10745 | 10175 | 9665 | 9195 | 8555 | 8000 | 7365 | 6700 |
| 150 | 13020 | 12630 | 11890 | 11215 | 10600 | 10035 | 9530 | 8870 | 8295 | 7625 | 6920 |
| 160 | 13685 | 13260 | 12440 | 11720 | 11050 | 10465 | 9930 | 9205 | 8595 | 7880 | 7140 |
| 170 | 14310 | 13835 | 12960 | 12180 | 11480 | 10845 | 10275 | 9530 | 8880 | 8130 | 7360 |
| 176 | 14680 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 180 | 14920 | 14405 | 13480 | 12650 | 11900 | 11225 | 10635 | 9855 | 9160 | 8380 | 7575 |
| 183 | 15100 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 185 | 15230 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 187·8 | 15400 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 190·0 | 15540 | 14985 | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 195 | 15870 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 200 | 16150 | 15550 | 14480 | 13525 | 12700 | 11980 | 11325 | 10460 | 9705 | 8870 | 8000 |
| 210 | 16760 | 16110 | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 220 | 17350 | 16690 | 15480 | 14445 | 13525 | 12730 | 12025 | 11075 | 10275 | 9380 | 8440 |
| 230 | 17950 | 17250 | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 240 | 18530 | 17800 | 16480 | 15340 | 14360 | 13475 | 12705 | 11700 | 10845 | 9875 | 8875 |
| 250 | 19100 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 260 | 19670 | 18880 | 17470 | 16210 | 15140 | 14210 | 13390 | 12330 | 11425 | 10380 | 9305 |
| 270 | 20250 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 280 | 20820 | 19970 | 18450 | 17120 | 15990 | 14995 | 14095 | 12960 | 11990 | 10920 | 9775 |

## Isochors, read from Isothermals.

| Vol. … | 50 | 60 | 70 | 80 | 90 | 100 | 120 | 140 | 160 | 180 | 200 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Temp. | Pressures. | | | | | | | | | | |
| 50° | … | … | … | … | … | … | … | … | … | 1438 | 1305 |
| 60 | … | … | … | … | … | … | … | 1880 | 1665 | 1491 | 1354 |
| 70 | … | … | … | … | … | 2633 | 2240 | 1947 | 1720 | 1544 | 1400 |
| 80 | … | … | … | 3321 | 3000 | 2738 | 2315 | 2015 | 1780 | 1594 | 1443 |
| 90 | … | … | 3865 | 3452 | 3110 | 2835 | 2400 | 2081 | 1837 | 1643 | 1489 |
| 100 | 5295 | 4575 | 4015 | 3565 | 3215 | 2932 | 2480 | 2152 | 1897 | 1695 | 1532 |
| 110 | 5510 | 4745 | 4150 | 3698 | 3327 | 3030 | 2558 | 2217 | 1953 | … | … |
| 120 | 5720 | 4910 | 4295 | 3820 | 3440 | 3117 | 2637 | 2283 | 2009 | 1796 | 1622 |
| 130 | 5930 | 5080 | 4435 | 3938 | 3537 | 3212 | 2711 | 2348 | 2062 | … | … |
| 140 | 6135 | 5240 | 4570 | 4055 | 3645 | 3303 | 2790 | 2413 | 2120 | 1896 | 1714 |
| 150 | 6330 | 5400 | 4715 | … | … | … | … | … | … | … | … |
| 160 | 6525 | 5560 | 4850 | 4295 | 3850 | 3492 | 2943 | 2545 | 2234 | 1995 | 1805 |
| 170 | 6725 | 5725 | 4990 | … | … | … | … | … | … | … | … |
| 180 | 6920 | 5880 | 5110 | 4522 | 4052 | 3667 | 3093 | 2666 | 2345 | 2096 | 1894 |
| 200 | 7290 | 6185 | 5375 | 4757 | 4257 | 3855 | 3240 | 2800 | 2458 | 2194 | 1981 |
| 220 | 7675 | 6500 | 5635 | 4993 | 4475 | 4043 | 3393 | 2926 | 2566 | 2290 | 2066 |
| 240 | 8060 | 6820 | 5905 | … | … | … | … | … | … | … | … |
| 250 | … | … | … | 5325 | 4765 | 4310 | 3622 | 3130 | 2739 | 2435 | 2200 |
| 260 | 8455 | 7145 | 6165 | … | … | … | … | … | … | … | … |
| 280 | 8850 | 7460 | 6450 | 5685 | 5085 | 4588 | 3848 | 3320 | 2907 | 2584 | 2334 |

## Isochors, read from Isothermals.

| Vol. … | 230 | 260 | 300 | 350 | 400 | 500 | 600 | 700 | 800 | 900 | 1000 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Temp. | Pressures. | | | | | | | | | | |
| 10·75° | … | … | … | … | … | … | 398 | 342·5 | 300 | 268 | 241·5 |
| 30 | … | … | … | 719 | 633·5 | 509 | 426 | 366·5 | 322 | 286·5 | 258·5 |
| 40 | 1105 | 985 | 860 | 743·5 | 654 | 526 | 440·5 | 380 | 333·5 | 296·5 | 267 |
| 50 | 1145 | 1020 | 890 | 769 | 675·5 | 544 | 454·5 | 391·5 | 344 | 305·5 | 275 |
| 60 | 1186 | 1054 | 917 | 795 | 699 | 561·5 | 470·5 | 404 | 355 | 316 | 284·5 |
| 70 | 1225 | 1092 | 952 | 820 | 720 | 580 | 484·5 | 416·5 | 365·5 | 325 | 293·5 |
| 80 | 1262 | 1124 | 979 | 844 | 743·5 | 596·5 | 500 | 429·5 | 376 | 335 | 302 |
| 90 | 1301 | 1158 | 1010 | 869 | 764·5 | 615 | 514 | 441·5 | 387·5 | 345 | 311 |
| 100 | 1343 | 1194 | 1038 | 895 | 787 | 634 | 528·5 | 454 | 398·5 | 354·5 | 319·5 |
| 110 | … | … | … | … | 809·5 | 650 | 543·5 | 467 | 409·5 | 364·5 | 328·5 |
| 120 | 1420 | 1262 | 1097 | 947 | 831 | 670 | 559·5 | 479·5 | 420·5 | 374 | 337 |
| 130 | … | … | … | … | 854·5 | 686 | 574 | 493 | 431·5 | 384 | 346 |
| 140 | 1497 | 1332 | 1156 | 995 | 876·0 | 704·5 | 588·5 | 505 | 443·5 | 395 | 355 |
| 150 | … | … | … | … | 899·5 | 723·5 | 604·5 | 518·5 | 454 | 403·5 | 363·5 |
| 160 | 1576 | 1400 | 1216 | 1046 | 916 | … | … | … | … | … | … |
| 180 | 1654 | 1467 | 1275 | 1095 | 964 | … | … | … | … | … | … |
| 200 | 1728 | 1535 | 1334 | 146 | 1005 | … | … | … | … | … | … |
| 220 | 1806 | 1603 | 1394 | 194 | 1047 | … | … | … | … | … | … |
| 250 | 1921 | 1706 | 1481 | 1272 | 1114 | … | … | … | … | … | … |
| 280 | 2036 | 1806 | 1568 | 1349 | 1182 | … | … | … | … | … | … |

Isochors, read from Isothermals.

| Vol. … | 1200 | 1400 | 1600 | 1800 | 2000 | 2300 | 2600 | 3000 | 3500 | 4000 |
|---|---|---|---|---|---|---|---|---|---|---|
| Temp. | Pressures. | | | | | | | | | |
| 10·75° | 202·0 | … | … | … | … | … | … | … | … | … |
| 11·0 | 202·0 | 173·5 | 151·8 | 135·1 | 121·8 | 106·2 | 94·2 | 81·6 | 70·0 | 61·3 |
| 16·3 | 205·5 | 177·0 | 154·9 | 137·8 | 124·0 | 108·1 | 95·8 | 83·0 | 71·4 | 62·4 |
| 30 | 215·8 | 185·5 | 162·4 | 144·4 | 130·1 | 113·5 | 100·6 | 87·3 | 74·7 | 65·3 |
| 40 | 223·0 | 191·5 | 168·0 | 149·8 | 134·8 | 117·3 | 104·1 | 90·4 | 77·5 | 67·7 |
| 50 | 230·0 | 197·5 | 173·3 | 154·3 | 139·2 | 121·0 | 107·2 | 93·3 | 79·9 | 69·8 |
| 60 | 237·3 | 204·2 | 178·7 | 158·9 | 143·1 | 124·7 | 110·3 | 96·0 | 82·2 | 71·8 |
| 70 | 245·0 | 210·0 | 184·0 | 163·4 | 147·5 | 128·7 | 113·8 | 98·8 | 84·8 | 74·2 |
| 80 | 251·6 | 215·7 | 189·4 | 168·4 | 151·8 | 132·1 | 117·2 | 101·9 | 87·3 | 76·2 |
| 90 | 259·2 | 223·5 | 195·3 | 173·9 | 156·6 | 136·1 | 120·7 | 105·1 | 89·9 | 78·5 |
| 100 | 266·7 | 229·7 | 200·9 | 179·0 | 160·7 | 140·0 | 124·3 | 108·0 | 92·4 | 80·4 |
| 110 | 273·5 | … | … | … | … | … | … | … | … | … |
| 120 | 280·5 | … | … | … | … | … | … | … | … | … |
| 130 | 288·5 | … | … | … | … | … | … | … | … | … |
| 140 | 296·0 | … | … | … | … | … | … | … | … | … |
| 150 | 303·0 | … | … | … | … | … | … | … | … | … |

The values of $\frac{dp}{dt}$ ($b$ in the equation $p=b\mathrm{T}-a$) have been calculated from the data given in the preceding tables, and as they are not quite constant at all volumes it seems necessary to give them in detail so as to indicate the nature of the variations. This, however, has not been done for volumes below 2·4 cub. centim., for which the values of $\frac{dp}{dt}$ were obtained from the isobars, because the deviations are within the limits of experimental error.

### Values of $\frac{dp}{dt}$ $(=b)$ from Isochors.

| Vol. … | 2·4 | 2·5 | 2·6 | 2·7 | 2·8 | 2·9 | 3·0 | 3·2 | 3·4 | 3·6 | 3·8 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Temp. | | | | | | | | | | | |
| 170° | | | | | | | | | | | |
| | 1243 | 1093 | … | … | … | … | … | … | … | … | … |
| 176 | | | | | | | | | | | |
| | 1220 | 1120 | 1005 | 850 | … | … | … | … | … | … | … |
| 180 | | | | | | | | | | | |
| | 1240 | 1073 | 960 | 863 | 767 | … | … | … | … | … | … |
| 183 | | | | | | | | | | | |
| | 1280 | 1100 | 1010 | 900 | 790 | 705 | 650 | … | … | … | … |
| 185 | | | | | | | | | | | |
| | 1214 | 1100 | 964 | 864 | 796 | 714 | 643 | … | … | … | … |
| 187·8 | | | | | | | | | | | |
| | 1327 | 1173 | 1045 | 909 | 814 | 750 | 636 | 577 | 518 | 464 | 423 |
| 190 | | | | | | | | | | | |
| | … | 1136 | 1008 | 918 | 830 | 756 | 720 | 602 | 534 | 478 | 446 |
| 195 | | | | | | | | | | | |
| | … | 1148 | 1032 | 926 | 844 | 766 | 710 | 618 | 544 | 498 | 458 |
| 200 | | | | | | | | | | | |
| | … | … | … | 930 | 834 | 776 | 708 | 624 | 554 | 512 | 468 |
| 205 | | | | | | | | | | | |
| | … | … | … | 970 | 886 | 790 | 722 | 620 | 566 | 502 | 464 |
| 210 | | | | | | | | | | | |
| | … | … | … | … | … | 792 | 747 | 648 | 568 | 515 | 477 |
| 220 | | | | | | | | | | | |
| | … | … | … | … | … | … | … | 653 | 592 | 529 | 477 |
| 230 | | | | | | | | | | | |
| | … | … | … | … | … | … | … | … | … | 543 | 501 |
| 240 | | | | | | | | | | | |

### Values of $\frac{dp}{dt}$ $(=b)$ from Isochors.

| Vol. … | 4·0 | 4·3 | 4·6 | 5·0 | 5·5 | 6·0 | 6·5 | 7·0 | 7·5 | 8·0 | 8·5 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Temp. | | | | | | | | | | | |
| 180° | | | | | | | | | | | |
| | … | … | … | … | … | … | … | … | … | 190 | 180 |
| 183 | | | | | | | | | | | |
| | … | … | … | … | … | … | … | … | 210 | 200 | 185 |
| 185 | | | | | | | | | | | |
| | … | … | … | … | … | … | 250 | 225 | 200 | 182 | 168 |
| 187·8 | | | | | | | | | | | |
| | 405 | 386 | 368 | 350 | 309 | 264 | 236 | 218 | 209 | 182 | 167 |
| 190 | | | | | | | | | | | |
| | 418 | 384 | 368 | 334 | 302 | 274 | 248 | 226 | 208 | 194 | 198 |
| 195 | | | | | | | | | | | |
| | 428 | 390 | 356 | 326 | 296 | 272 | 242 | 222 | 200 | 186 | 168 |
| 200 | | | | | | | | | | | |
| | 434 | 400 | 366 | 336 | 292 | 262 | 242 | 224 | { 196 | 181 | 168 |
| 205 | | | | | | | | | | | |
| | 430 | 390 | 362 | 322 | 294 | 260 | 234 | 212 | | | |
| 210 | | | | | | | | | | | |
| | 443 | 396 | 357 | 323 | 288 | 259 | 233 | 210 | 193 | 178 | 164 |
| 220 | | | | | | | | | | | |
| | 439 | 395 | 364 | 327 | 287 | 257 | 234 | 212 | 194 | 177 | 165 |
| 230 | | | | | | | | | | | |
| | 462 | 418 | 373 | 328 | 288 | 258 | 232 | 211 | 193 | 177 | 163 |
| 240 | | | | | | | | | | | |
| | 446 | 400 | 373 | 331 | 287 | 252 | 227 | 207 | 191 | 176 | 163 |
| 250 | | | | | | | | | | | |
| | … | 403 | 364 | 324 | 286 | 251 | 221 | 201 | 184 | 170 | 156 |
| 260 | | | | | | | | | | | |
| | … | … | … | 323 | 286 | 254 | 230 | 208 | 190 | 176 | 164 |
| 270 | | | | | | | | | | | |
| | … | … | … | … | 279 | 251 | 222 | 198 | 179 | 164 | 152 |
| 280 | | | | | | | | | | | |

## Values of $\frac{dp}{dt}$ $(=b)$ from Isochors.

| Vol. ... | 9·0 | 9·5 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Temp. | | | | | | | | | | | |
| 150° | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 71 |
| 160 | ... | ... | ... | ... | ... | ... | 92 | 87 | 79 | 71 | 67·5 |
| 170 | ... | ... | ... | 126 | 114 | 102 | 93 | 83 | 77 | 71 | 65·5 |
| 180 | 172 | 158 | 148 | 132 | 114 | 104 | 94 | 86 | 78 | 76 | 68 |
| 185 | 152 | 146 | 134 | 114 | 104 | 92 | 86 | 80 | 76 | 72 | 64 |
| 190 | 166 | 150 | 140 | 124 | 108 | 98 | 88 | 80 | 74 | 66 | 68 |
| 195 | 158 | 148 | 140 | 124 | 114 | 102 | 92 | 84 | 74 | 70 | 66 |
| 200 | 156 | 146 | 135 | 120 | 105 | 96 | 86 | 81 | 75 | 68 | 63 |
| 210 | 152 | 140 | 132 | 117 | 105 | 95 | 89 | 79 | 72 | 69 | 62 |
| 220 | 153 | 143 | 132 | 115 | 106 | 93 | 84 | 78 | 72 | 67 | 64 |
| 230 | 151 | 141 | 134 | 120 | 106 | 95 | 85 | 78 | 74 | 68 | 64 |
| 240 | 152 | 142 | 132 | 117 | 101 | 96 | 87 | 81 | 73 | 67 | 61 |
| 250 | 146 | 136 | 128 | 113 | 104 | 91 | 85 | 76 | 72 | 66 | 60 |
| 260 | 149 | 139 | 131 | 117 | 104 | 93 | 84 | 78 | 70 | 65 | 61 |
| 270 | 146 | 135 | 124 | 108 | 99 | 89 | 81 | 74 | 71 | 65 | 62 |
| 280 | | | | | | | | | | | |

## Values of $\frac{dp}{dt}$ $(=b)$ from Isochors.

| Vol.... | 19 | 20 | 22 | 24 | 26 | 28 | 30 | 33 | 36 | 40 | 45 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Temp. | | | | | | | | | | | |
| 110° | ... | ... | ... | ... | ... | ... | ... | ... | ... | 26 | 24 |
| 120 | ... | ... | ... | ... | ... | ... | ... | 33 | 30·5 | 27 | 23 |
| 130 | ... | ... | ... | ... | ... | 41·5 | 37 | 33·5 | 29·5 | 26·5 | 23·5 |
| 140 | ... | ... | 53·5 | 47 | 42·5 | 37 | 33·5 | 31·5 | 29·5 | 26 | 22 |
| 150 | 66·5 | 63 | 55 | 50·5 | 45 | 43 | 40 | 33·5 | 30 | 25·5 | 22 |
| 160 | 62·5 | 57·5 | 52 | 46 | 43 | 38 | 34·5 | 32·5 | 28·5 | 25 | 22 |
| 170 | 61 | 57 | 52 | 47 | 42 | 38 | 36 | 32·5 | 28 | 25 | 21·5 |
| 180 | 62 | 58 | 50 | 43·7 | 45 | 37·8 | 34·5 | 30·2 | 27·8 | 24·5 | 21·2 |
| 190 | 61 | 56·5 | | | | | | | | | |
| 200 | 61 | 56 | 50 | 46 | 41·2 | 37·5 | 35 | 30·8 | 28·5 | 25·5 | 22 |
| 210 | 59 | 58 | | | | | | | | | |
| 220 | 60 | 56 | 50 | 44·8 | 41·8 | 37·2 | 34 | 31·2 | 28·5 | 24·8 | 21·8 |
| 230 | 58 | 55 | | | | | | | | | |
| 240 | 57 | 54 | 49·5 | 43·5 | 39 | 36·8 | 34·8 | 31·5 | 29 | 25·2 | 21·5 |
| 250 | 57 | | | | | | | | | | |
| 260 | 58 | 54·5 | 49 | 45·5 | 42·5 | 39·7 | 35·2 | 31·5 | 28·2 | 27 | 23·5 |
| 270 | 57 | | | | | | | | | | |
| 280 | | | | | | | | | | | |

Values of $\frac{dp}{dt}$ $(=b)$ from Isochors.

| Vol.... | 50 | 60 | 70 | 80 | 90 | 100 | 120 | 140 | 160 | 180 | 200 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Temp. | | | | | | | | | | | |
| 50° | | | | | | | | | | | |
| | ... | ... | ... | ... | ... | ... | ... | ... | ... | 5·3 | 4·9 |
| 60 | | | | | | | | | | | |
| | ... | ... | ... | ... | ... | ... | ... | 6·7 | 5·5 | 5·3 | 4·6 |
| 70 | | | | | | | | | | | |
| | ... | ... | ... | ... | ... | 10·5 | 7·5 | 6·8 | 6·0 | 5·0 | 4·3 |
| 80 | | | | | | | | | | | |
| | ... | ... | ... | 13·1 | 11·0 | 9·7 | 8·5 | 6·6 | 5·7 | 4·9 | 4·6 |
| 90 | | | | | | | | | | | |
| | ... | ... | 15·0 | 11·3 | 10·5 | 9·7 | 8·0 | 7·1 | 6·0 | 5·2 | 4·3 |
| 100 | | | | | | | | | | | |
| | 21·5 | 17·0 | 13·5 | 13·3 | 11·2 | 9·8 | 7·8 | 6·5 | 5·6 | | |
| 110 | | | | | | | | | | 5·05 | 4·5 |
| | 21·0 | 16·5 | 14·5 | 12·2 | 11·3 | 9·7 | 7·9 | 6·6 | 5·6 | | |
| 120 | | | | | | | | | | | |
| | 21·0 | 17·0 | 14·0 | 11·8 | 9·7 | 9·5 | 7·4 | 6·5 | 5·3 | | |
| 130 | | | | | | | | | | 5·0 | 4·6 |
| | 20·5 | 16·0 | 13·5 | 11·7 | 10·8 | 9·1 | 7·9 | 6·5 | 5·8 | | |
| 140 | | | | | | | | | | | |
| | 19·5 | 16·0 | 14·5 | | | | | | | | |
| 150 | | | | 12·0 | 10·25 | 9·45 | 7·65 | 6·6 | 5·7 | 4·95 | 4·55 |
| | 19·5 | 16·0 | 13·5 | | | | | | | | |
| 160 | | | | | | | | | | | |
| | 20·0 | 16·5 | 14·0 | | | | | | | | |
| 170 | | | | 11·35 | 10·1 | 8·75 | 7·5 | 6·05 | 5·55 | 5·05 | 4·45 |
| | 19·5 | 15·5 | 12·0 | | | | | | | | |
| 180 | | | | | | | | | | | |
| | 18·5 | 15·25 | 13·25 | 11·75 | 10·25 | 9·4 | 7·35 | 6·7 | 5·65 | 4·9 | 4·35 |
| 200 | | | | | | | | | | | |
| | 19·25 | 15·75 | 13·0 | 11·8 | 10·9 | 9·4 | 7·65 | 6·3 | 5·4 | 4·8 | 4·25 |
| 220 | | | | | | | | | | | |
| | 19·25 | 16·0 | 13·5 | | | | | | | | |
| 240 | | | | 11·07 | 9·67 | 8·9 | 7·63 | 6·8 | 5·77 | 4·83 | 4·47 |
| | 19·75 | | | | | | | | | | |
| 250 | ... | 16·25 | 13·0 | | | | | | | | |
| 260 | | | | 12·0 | 10·67 | 9·25 | 7·53 | 6·33 | 5·6 | 4·97 | 4·47 |
| | 19·75 | 15·75 | 14·25 | | | | | | | | |
| 280 | | | | | | | | | | | |

### Values of $\frac{dp}{dt}$ $(=b)$ from Isochors.

| Vol.… | 230 | 260 | 300 | 350 | 400 | 500 | 600 | 700 | 800 | 900 | 1000 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Temp. | | | | | | | | | | | |
| 10°·75 | | | | | | | | | | | |
| 11 | | | | | | | | | | | |
| | | | | | | | 1·45 | 1·25 | 1·14 | ·96 | ·88 |
| 16·3 | | | | | | | | | | | |
| 30 | | | | | | | | | | | |
| | … | … | … | 2·45 | 2·05 | 1·7 | 1·45 | 1·35 | 1·15 | 1·0 | ·85 |
| 40 | | | | | | | | | | | |
| | 4·0 | 3·5 | 3·0 | 2·55 | 2·15 | 1·8 | 1·4 | 1·15 | 1·05 | ·9 | ·9 |
| 50 | | | | | | | | | | | |
| | 4·1 | 3·4 | 2·7 | 2·6 | 2·35 | 1·75 | 1·6 | 1·25 | 1·1 | 1·05 | ·95 |
| 60 | | | | | | | | | | | |
| | 3·9 | 3·8 | 3·5 | 2·5 | 2·1 | 1·85 | 1·4 | 1·25 | 1·05 | ·9 | ·9 |
| 70 | | | | | | | | | | | |
| | 3·7 | 3·2 | 2·7 | 2·4 | 2·35 | 1·65 | 1·55 | 1·3 | 1·05 | 1·0 | ·85 |
| 80 | | | | | | | | | | | |
| | 3·9 | 3·4 | 3·1 | 2·5 | 2·1 | 1·85 | 1·4 | 1·2 | 1·15 | 1·0 | ·9 |
| 90 | | | | | | | | | | | |
| | 4·2 | 3·6 | 2·8 | 2·6 | 2·25 | 1·9 | 1·45 | 1·25 | 1·1 | ·95 | ·85 |
| 100 | | | | | | | | | | | |
| | | | | | 2·25 | 1·6 | 1·5 | 1·3 | 1·1 | 1·0 | ·9 |
| 110 | 3·85 | 3·4 | 2·95 | 2·6 | | | | | | | |
| | | | | | 2·15 | 2·0 | 1·6 | 1·25 | 1·1 | ·95 | ·85 |
| 120 | | | | | | | | | | | |
| | | | | | 2·35 | 1·6 | 1·45 | 1·35 | 1·1 | 1·0 | ·9 |
| 130 | | | | | | | | | | | |
| | 3·85 | 3·5 | 2·95 | 2·4 | 2·15 | 1·85 | 1·45 | 1·2 | 1·2 | 1·1 | ·9 |
| 140 | | | | | | | | | | | |
| | | | | | 2·35 | 1·9 | 1·6 | 1·35 | 1·05 | ·85 | ·85 |
| 150 | | | | | | | | | | | |
| | 3·95 | 3·4 | 3·0 | 2·55 | 1·65 | … | … | … | … | … | … |
| 160 | | | | | | | | | | | |
| | 3·9 | 3·35 | 2·95 | 2·45 | 2·4 | … | … | … | … | … | … |
| 180 | | | | | | | | | | | |
| | 3·7 | 3·4 | 2·95 | 2·55 | 2·05 | … | … | … | … | … | … |
| 200 | | | | | | | | | | | |
| | 3·9 | 3·4 | 3·0 | 2·4 | 2·1 | … | … | … | … | … | … |
| 220 | | | | | | | | | | | |
| | 3·83 | 3·43 | 2·9 | 2·6 | 2·23 | … | … | … | … | … | … |
| 250 | | | | | | | | | | | |
| | 3·83 | 3·33 | 2·9 | 2·57 | 2·27 | … | … | … | … | … | … |
| 280 | | | | | | | | | | | |

Values of $\frac{dp}{dt}(=b)$ from Isochors.

| Vol. ... | 1200 | 1400 | 1600 | 1800 | 2000 | 2300 | 2600 | 3000 | 3500 | 4000 |
|---|---|---|---|---|---|---|---|---|---|---|
| Temp. | | | | | | | | | | |
| 10°·75 | ·64 | | | | | | | | | |
| 11·0 | | ·66 | | | | | | | | |
| 16·3 | | | ·58 | ·51 | ·42 | ·36 | ·30 | ·26 | ·26 | ·21 |
| 30 | ·75 | ·62 | ·55 | ·50 | ·45 | ·39 | ·35 | ·31 | ·24 | ·21 |
| 40 | ·72 | ·60 | ·56 | ·54 | ·47 | ·38 | ·35 | ·31 | ·28 | ·24 |
| 50 | ·70 | ·60 | ·53 | ·45 | ·44 | ·37 | ·31 | ·29 | ·24 | ·21 |
| 60 | ·73 | ·67 | ·54 | ·46 | ·39 | ·37 | ·31 | ·27 | ·23 | ·20 |
| 70 | ·77 | ·58 | ·53 | ·45 | ·44 | ·40 | ·35 | ·28 | ·26 | ·24 |
| 80 | ·66 | ·57 | ·54 | ·50 | ·43 | ·34 | ·34 | ·31 | ·25 | ·20 |
| 90 | ·76 | ·78 | ·59 | ·55 | ·48 | ·40 | ·35 | ·32 | ·26 | ·23 |
| 100 | ·75 | ·62 | ·56 | ·51 | ·41 | ·39 | ·36 | ·29 | ·25 | ·19 |
| 110 | ·68 | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 120 | ·70 | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 130 | ·80 | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 140 | ·75 | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 150 | ·70 | ... | ... | ... | ... | ... | ... | ... | ... | ... |

It will be seen from the preceding tables that the values of $\frac{dp}{dt}(=b)$ are nearly but not quite constant. At volumes lower than 4·6 cub. centim. (the critical volume of a gram =4·266 cub. centim.) the values of $b$ increase with rise of temperature, whilst at greater volumes (up to about 400 cub. centim.) they diminish. At still larger volumes they appear to be constant, at any rate the deviations are within the limits of experimental error.

These deviations of $b$ from constancy appear to be far too regular to be attributed to experimental error, and the results seem to confirm the conclusion arrived at by Amagat in the case of the substances examined by him, that the values of $b$ are not absolutely constant.

It is noteworthy that with isopentane the isochor for a volume very slightly higher than the critical volume is straight, whilst those on either side are slightly curved in opposite directions.

It is also noticeable that the variations in the values of *b* diminish as the temperature rises, and, indeed, that at volumes higher than 30 cub. centim. they practically disappear at the higher temperatures.

This also agrees with Amagat's conclusions from his observations with carbon dioxide, ethylene, and other gases ("Mémoires sur l'élasticité et la dilatabilité des Fluides jusqu' aux très hautes Pressions," *Ann. Chim. Phys.* 6th Series, vol. xxix. p. 67) :—"Il parait résulter de l'ensemble de ces résultats que les variations du coefficient de pression avec la température, *toujours très petites*, s'annulent aux températures suffisamment élevées et probablement à toutes les températures, sous des pressions suffisantes ; c'est bien ce que paraissent montrer les résultats relatifs à ceux des gaz qui, dans les limites de température de ce travail, sont déjà beaucoup au-dessus de leur température critique."

The temperatures and pressures at the volumes given in the tables were mapped, and straight lines drawn to pass as well as possible through the points. From these straight lines the values of *b* were obtained, and they are given in the following table (pp. 650, 651). As the values of *b* tend to become constant at high temperatures, they have also been calculated for volumes from 2·4 to 400 cub. centim. from the observations at the three highest temperatures, and these are also given.

At lower volumes than 2·4 cub. centim. the isochors were obtained indirectly from the isobars, and at higher volumes than 400 cub. centim. the variations are within the limits of experimental error.

The values of *b* cannot well be mapped against the volume, but I have adopted the suggestion of Rose-Innes and plotted the values of $\frac{10000}{bv}$ against $v^{-1/3}$ (fig. 3, p. 652).

At the largest volumes the value of $\frac{10000}{bv}$ becomes very nearly constant and agrees closely with that (11·6) calculated from the molecular weight of isopentane.

| | $b$. | | $\frac{10000}{bv}$. | |
|---|---|---|---|---|
| Volume of a gram in cub. centim. | From drawn Isochors. | From observations at three highest temperatures. | From drawn Isochors. | From observations at three highest temperatures. |
| 1·58 | 5711 | …… | 1·108 | …… |
| 1·6 | 5450 | …… | 1·147 | …… |
| 1·65 | 4823 | …… | 1·257 | …… |
| 1·7 | 4202 | …… | 1·400 | …… |
| 1·75 | 3712 | …… | 1·540 | …… |
| 1·8 | 3390 | …… | 1·639 | …… |
| 1·85 | 3014 | …… | 1·794 | …… |
| 1·9 | 2734 | …… | 1·925 | …… |
| 1·95 | 2475 | …… | 2·072 | …… |
| 2·0 | 2309 | …… | 2·165 | …… |
| 2·1 | 1914 | …… | 2·487 | …… |
| 2·2 | 1644 | …… | 2·764 | …… |
| 2·3 | 1425 | …… | 3·051 | …… |
| 2·4 | 1238 | 1274 | 3·365 | 3·27 |
| 2·5 | 1111 | 1152 | 3·602 | 3·47 |
| 2·6 | 998·5 | 1028 | 3·851 | 3·74 |
| 2·7 | 913·0 | 942 | 4·056 | 3·93 |
| 2·8 | 834·5 | 855 | 4·279 | 4·18 |
| 2·9 | 763·0 | 786 | 4·520 | 4·39 |
| 3·0 | 704·5 | 726 | 4·731 | 4·59 |
| 3·2 | 627·0 | 640 | 4·986 | 4·88 |
| 3·4 | 557·0 | 575 | 5·281 | 5·12 |
| 3·6 | 509·5 | 529 | 5·455 | 5·25 |
| 3·8 | 468·0 | 485 | 5·507 | 5·43 |
| 4·0 | 436·0 | 449 | 5·733 | 5·57 |
| 4·3 | 397·0 | 407 | 5·859 | 5·71 |
| 4·6 | 363·9 | 370 | 5·973 | 5·88 |
| 5·0 | 327·1 | 326 | 6·114 | 6·14 |
| 5·5 | 288·7 | 284 | 6·298 | 6·40 |
| 6·0 | 256·8 | 252 | 6·489 | 6·61 |
| 6·5 | 232·1 | 224 | 6·628 | 6·87 |
| 7·0 | 210·5 | 202 | 6·786 | 7·07 |
| 7·5 | 192 6 | 184 | 6·925 | 7·25 |
| 8·0 | 177·4 | 170 | 7·046 | 7·35 |
| 8·5 | 164·3 | 157 | 7·195 | 7·49 |
| 9·0 | 152·3 | 147 | 7·294 | 7·56 |
| 9·5 | 141·8 | 137 | 7·424 | 7·68 |
| 10 | 132·6 | 128 | 7·541 | 7·81 |
| 11 | 118·0 | 112·7 | 7·705 | 8·07 |
| 12 | 105·3 | 102·3 | 7·917 | 8·15 |
| 13 | 95·11 | 91·0 | 8·088 | 8·45 |
| 14 | 86·67 | 83·3 | 8·258 | 8·58 |
| 15 | 79 37 | 76·0 | 8·400 | 8·77 |
| 16 | 73·86 | 71·0 | 8·463 | 8·80 |
| 17 | 68·26 | 65·3 | 8·618 | 9·01 |
| 18 | 63·31 | 61·0 | 8·698 | 9·11 |
| 19 | 59·63 | 57·3 | 8·835 | 9·18 |
| 20 | 56·36 | 54·5 | 8·872 | 9·18 |
| 22 | 50·62 | 49·5 | 8·979 | 9·18 |
| 24 | 45·31 | 44·6 | 9·196 | 9·34 |
| 26 | 41·30 | 41·1 | 9 314 | 9·36 |
| 28 | 38·11 | 37·9 | 9·372 | 9·42 |
| 30 | 35·20 | 34·7 | 9·470 | 9·61 |
| 33 | 31·77 | 31·4 | 9·539 | 9·65 |
| 36 | 28·57 | 28·6 | 9·722 | 9·71 |

Table (*continued*).

| | *b.* | | $\frac{10000}{bv}$. | |
|---|---|---|---|---|
| Vol. of gram in c.c. | From drawn Isochors. | Obs. at 3 highest temps. | From drawn Isochors. | Obs. at 3 highest temps. |
| 40 | 25·48 | 25·7 | 9·813 | 9·73 |
| 45 | 22·03 | 22·3 | 10·09 | 9·97 |
| 50 | 19·49 | 19·6 | 10·26 | 10·21 |
| 60 | 15·94 | 16·0 | 10·46 | 10·42 |
| 70 | 13·56 | 13·6 | 10·53 | 10·50 |
| 80 | 11·92 | 11·62 | 10·49 | 10·76 |
| 90 | 10·47 | 10·41 | 10·61 | 10·67 |
| 100 | 9·31 | 9·18 | 10·74 | 10·89 |
| 120 | 7·66 | 7·60 | 10·87 | 10·97 |
| 140 | 6·54 | 6·48 | 10·92 | 11·02 |
| 160 | 5·64 | 5·59 | 11·07 | 11·18 |
| 180 | 4·97 | 4·87 | 11·18 | 11·41 |
| 200 | 4·45 | 4·40 | 11·24 | 11·36 |
| 230 | 3·887 | 3·85 | 11·18 | 11·29 |
| 260 | 3·427 | 3·39 | 11·22 | 11·35 |
| 300 | 2·957 | 2·93 | 11·27 | 11·38 |
| 350 | 2·521 | 2·52 | 11·33 | 11·34 |
| 400 | 2·188<br>2·222 | 2·20 | 11·43<br>11·25 | 11·36<br>…… |
| 500 | 1·792 | …… | 11·16 | …… |
| 600 | 1·485 | …… | 11·22 | …… |
| 700 | 1·261 | …… | 11·33 | …… |
| 800 | 1·095 | …… | 11·42 | …… |
| 900 | 0·977 | …… | 11·37 | …… |
| 1000 | 0·881 | …… | 11·35 | …… |
| 1200 | 0·727 | …… | 11·45 | …… |
| 1400 | 0·626 | …… | 11·41 | …… |
| 1600 | 0·549 | …… | 11·37 | …… |
| 1800 | 0·483 | …… | 11·51 | …… |
| 2000 | 0·437 | …… | 11·45 | …… |
| 2300 | 0·377 | …… | 11·53 | …… |
| 2600 | 0·332 | …… | 11·58 | …… |
| 3000 | 0·292 | …… | 11·40 | …… |
| 3500 | 0·251 | …… | 11·39 | …… |
| 4000 | 0·216 | …… | 11·58 | …… |

A curve drawn through the points obtained from the drawn isochors shows a decided hump in the neighbourhood of the critical volume, and, in this respect, resembles that constructed from the data obtained by Ramsay and myself with ether. With the values of $\frac{10000}{bv}$ calculated from the observations at the highest temperatures the hump becomes far less marked but does not disappear ; with the values derived from the observations at the lowest temperatures it would be greatly exaggerated.

It is possible that at still higher temperatures the curve might become quite smooth, but unfortunately above 280°

Fig. 3.

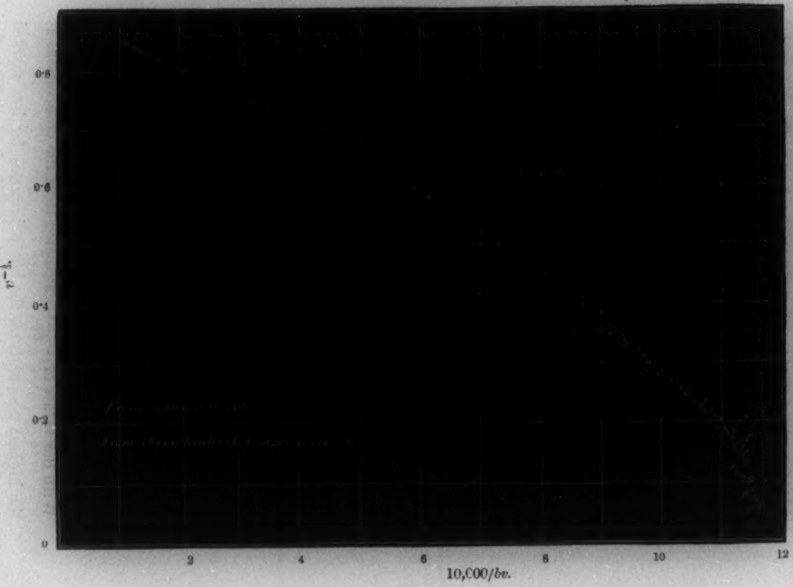
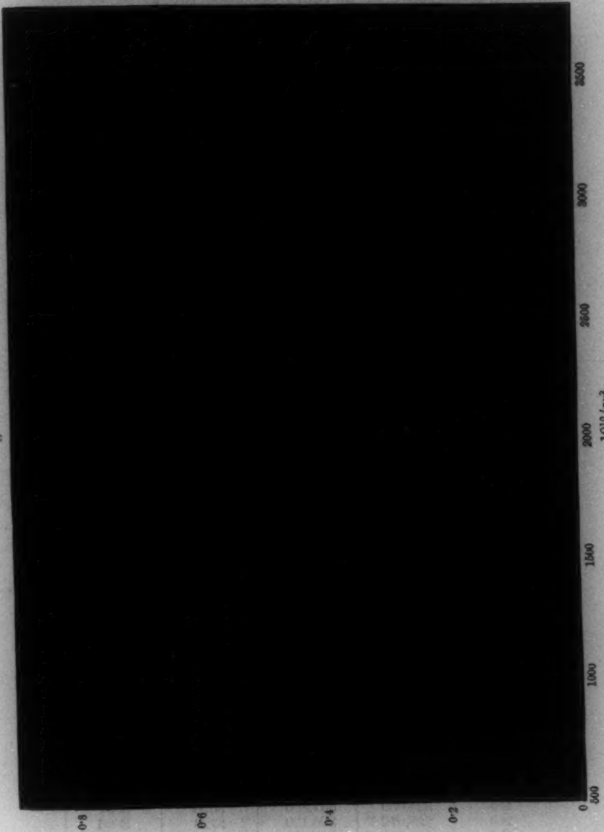

0·8
0·6
0·4
0·2
0
$v^{-\frac{1}{4}}$
2
4
6
8
10
12
10,000/*bv*.
From three highest temperatures ×

Fig. 4.



the vapour-pressure of mercury becomes too great to allow of accurate observations being made.

The values of $a$ in the equation $p=b\mathrm{T}-a$ were ascertained from the drawn isochors, and are given in the table below; also the values of $a$ calculated from those of $b$ derived from the observations at the three highest temperatures. In the latter case, whilst the slope of the isochor depends only on the results obtained at the highest temperatures, the whole of the observations were taken into account in determining its position, and therefore the value of $a$.

In mapping the values of $a$ it was found best, as suggested by Rose-Innes, to plot $\frac{10^{10}}{av^2}$ against $v^{-\frac{1}{3}}$. The curve is given in fig. 4 (p. 653), and the data in the following table.

It will be seen that a maximum is reached at about volume 3·2, and in this respect also the isopentane results show a strong resemblance to those with ether, the maximum for that substance being at about the same volume.

| $a$. | | | $\frac{10^{10}}{av^2}$. | |
|---|---|---|---|---|
| Volume of a gram in cub. centim. | From drawn Isochors. | From $b$'s from three highest temperatures. | From drawn Isochors. | From $b$'s from three highest temperatures. |
| 1·58 | 1,595,000 | ...... | 2511 | ...... |
| 1·6 | 1,566,800 | ...... | 2493 | ...... |
| 1·65 | 1,476,000 | ...... | 2489 | ...... |
| 1·7 | 1,355,200 | ...... | 2553 | ...... |
| 1·75 | 1,252,300 | ...... | 2607 | ...... |
| 1·8 | 1,189,000 | ...... | 2596 | ...... |
| 1·85 | 1,091,200 | ...... | 2678 | ...... |
| 1·9 | 1,017,400 | ...... | 2723 | ...... |
| 1·95 | 943,300 | ...... | 2788 | ...... |
| 2·0 | 898,400 | ...... | 2783 | ...... |
| 2·1 | 768,200 | ...... | 2952 | ...... |
| 2·2 | 676,700 | ...... | 3053 | ...... |
| 2·3 | 594,300 | ...... | 3181 | ...... |
| 2·4 | 521,550 | 537,640 | 3329 | 3229 |
| 2·5 | 471,000 | 489,930 | 3397 | 3266 |
| 2·6 | 425,050 | 438,550 | 3480 | 3373 |
| 2·7 | 389,450 | 402,590 | 3522 | 3407 |
| 2·8 | 355,650 | 365,010 | 3586 | 3494 |
| 2·9 | 324,030 | 334,850 | 3670 | 3551 |
| 3·0 | 298,070 | 308,120 | 3728 | 3606 |
| 3·2 | 263,340 | 269,700 | 3708 | 3621 |
| 3·4 | 231,520 | 240,200 | 3736 | 3601 |
| 3·6 | 209,590 | 219,230 | 3682 | 3520 |
| 3·8 | 190,690 | 198,930 | 3632 | 3481 |
| 4·0 | 175,900 | 182,310 | 3553 | 3428 |
| 4·3 | 157,880 | 162,890 | 3426 | 3320 |
| 4·6 | 142,630 | 145,690 | 3313 | 3244 |
| 5·0 | 125,630 | 125,150 | 3184 | 3196 |
| 5·5 | 107,960 | 105,650 | 3062 | 3129 |

|  | $a$. |  | $10^{10}/av^2$. |  |
|---|---|---|---|---|
| Vol. of gram in c.c. | From drawn Isochors. | From *b*'s fr. 3 highest temps. | From drawn Isochors. | From *b*'s fr. 3 highest temps. |
| 6 | 93,330 | 90,940 | 2976 | 3055 |
| 6·5 | 82,150 | 78,160 | 2881 | 3028 |
| 7 | 72,485 | 68,240 | 2816 | 2991 |
| 7·5 | 64,560 | 60,315 | 2754 | 2947 |
| 8 | 57,940 | 54,311 | 2697 | 2877 |
| 8·5 | 52,322 | 48,787 | 2645 | 2837 |
| 9 | 47,219 | 44,599 | 2615 | 2768 |
| 9·5 | 42,945 | 40,452 | 2580 | 2739 |
| 10 | 39,001 | 36,754 | 2564 | 2721 |
| 11 | 33,192 | 30,732 | 2490 | 2689 |
| 12 | 28,158 | 26,590 | 2466 | 2612 |
| 13 | 24,310 | 22,320 | 2434 | 2651 |
| 14 | 21,211 | 19,621 | 2405 | 2600 |
| 15 | 18,619 | 16,998 | 2386 | 2615 |
| 16 | 16,790 | 15,427 | 2327 | 2532 |
| 17 | 14,864 | 13,406 | 2328 | 2581 |
| 18 | 13,488 | 12,120 | 2288 | 2547 |
| 19 | 12,073 | 10,995 | 2295 | 2519 |
| 20 | 11,149 | 10,257 | 2242 | 2437 |
| 22 | 9511 | 8982 | 2172 | 2300 |
| 24 | 7912 | 7597 | 2194 | 2285 |
| 26 | 6848 | 6759 | 2160 | 2189 |
| 28 | 6070 | 5978 | 2101 | 2139 |
| 30 | 5345 | 5114 | 2079 | 2173 |
| 33 | 4592 | 4419 | 2000 | 2078 |
| 36 | 3814 | 3830 | 2023 | 2015 |
| 40 | 3174 | 3284 | 1969 | 1903 |
| 45 | 2423 | 2550 | 2038 | 1937 |
| 50 | 1935 | 1986 | 2067 | 2014 |
| 60 | 1358 | 1388 | 2046 | 2001 |
| 70 | 1043 | 1065 | 1957 | 1916 |
| 80 | 874 | 755 | 1788 | 2070 |
| 90 | 693 | 670 | 1782 | 1843 |
| 100 | 542 | 496 | 1845 | 2016 |
| 120 | 381 | 357 | 1823 | 1945 |
| 140 | 292 | 270 | 1747 | 1889 |
| 160 | 210 | 189 | 1860 | 2067 |
| 180 | 160 | 119 | 1930 | 2594 |
| 200 | 128 | 105 | 1950 | 2381 |
| 230 | 109 | 95 | 1730 | 1990 |
| 260 | 87 | 71 | 1700 | 2088 |
| 300 | 66 | 54 | 1680 | 2058 |
| 350 | 46 | 45 | 1770 | 1814 |
| 400 | 29 | 35·2 | 2150 | 1776 |
| 500 | 34·2 | ...... | 1170 | ...... |
| 600 | 23·9 | ...... | 1160 | ...... |
| 700 | 15·3 | ...... | 1330 | ...... |
| 800 | 8·9 | ...... | 1760 | ...... |
| 900 | 9·4 | ...... | 1310 | ...... |
| 1000 | 8·35 | ...... | 1980 | ...... |
| 1200 | 4·1 | ...... | 1690 | ...... |
| 1400 | 4·2 | ...... | 1210 | ...... |
| 1600 | 4·2 | ...... | 930 | ...... |
| 1800 | 1·9 | ...... | 1620 | ...... |
| 2000 | 2·4 | ...... | 1040 | ...... |
| 2300 | 0·9 | ...... | 2100 | ...... |
| 2600 | 0 | ...... | ...... | ...... |
| 3000 | 1·2 | ...... | 930 | ...... |
| 3500 | 1·2 | ...... | 680 | ...... |
| 4000 | 0 | ...... | ...... | ...... |

### *Comparison of Isopentane with other Substances at "Corresponding" Pressures.*

The absolute temperatures (boiling-points) and molecular volumes of liquid and saturated vapour were read from the curves at pressures "corresponding" to those adopted in previous papers on this subject (Phil. Mag. Feb. 1892, p. 153; Trans. Chem. Soc. lxiii. p. 1191; Phil. Mag. Jan. 1894, p. 1); and are given in the table below:—

| Ratio of Pressure to Critical Pressure. | Pressure. | Absolute Temperature. | Molecular Volume. | |
|---|---|---|---|---|
| | | | Liquid. | Saturated Vapour. |
| | millim. | | cub. centim. | cub. centim. |
| ·002949 | 73·8 | 247°·25 | ...... | ...... |
| ·005898 | 147·5 | 260·8 | ...... | ...... |
| ·011795 | 295·1 | 276·2 | 112·94 | ...... |
| ·022411 | 560·7 | 292·4 | 115·86 | 31040 |
| ·044232 | 1107 | 312·3 | 119·84 | 16380 |
| ·088465 | 2213 | 336·0 | 125·24 | 8490 |
| ·14744 | 3689 | 356·3 | 130·68 | 5180 |
| ·20642 | 5165 | 371·35 | 135·50 | 3675 |
| ·29488 | 7378 | 388·65 | 140·29 | 2540 |
| ·44232 | 11040 | 410·2 | 152·93 | 1614 |
| ·58978 | 14755 | 426·95 | 165·15 | 1132 |
| ·73721 | 18445 | 440·8 | 180·35 | 813·5 |
| ·82568 | 20660 | 448·0 | 192·35 | 671·5 |
| ·88465 | 22130 | 451·6 | 204·05 | 580·0 |
| ·94363 | 23610 | 457·0 | 221·65 | 482·5 |
| ·97313 | 24350 | 459·1 | 237·7 | 425·5 |
| 1·00000 | 25020 | 460·8 | 306·5 | 306·5 |

The ratios of the absolute temperatures and of the volumes to the critical constants show that isopentane belongs to the same group as benzene and its halogen derivatives, ether, carbon tetrachloride, and stannic chloride. The actual values approach most closely to those of benzene, and for the sake of comparison both are given in the following table (p. 657).

The ratios of the actual to the theoretical densities of the saturated vapour for isopentane and benzene are also given. At the critical point the ratio is 3·73, agreeing very closely with those for the other substances in group I. (3·65 to 3·83) and also with the ratio for carbon dioxide (3·62) deduced from Amagat's observations.

From these results it may be concluded that the molecules of liquid isopentane are simple, like those of the gas.

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*Errata* (p. 650).

$$\text{Values of } \frac{10000}{bv} \text{ at } \left\{ \begin{array}{llllll} \text{Volume} & 3\cdot8 & \textit{for} & 5\cdot507 & \textit{read} & 5\cdot623 \\ \;\;\;\text{,,} & 8\cdot5 & \text{,,} & 7\cdot195 & \text{,,} & 7\cdot160 \\ \;\;\;\text{,,} & 14 & \text{,,} & 8\cdot258 & \text{,,} & 8\cdot241 \end{array} \right.$$

| Ratio of Pressure to Critical Pressure. | $\frac{\text{Absolute Temperature}}{\text{Abs. Critical Temperature}}$. | | $\frac{\text{Mol. Vol. of Liquid}}{\text{Mol. Critical Volume}}$. | | $\frac{\text{Mol. Vol. Sat. Vapour}}{\text{Mol. Critical Volume}}$. | | $\frac{\text{Actual Density Sat. Vap.}}{\text{Theoretical Density.}}$. | |
|---|---|---|---|---|---|---|---|---|
| | Isopentane. | Benzene. | Isopentane. | Benzene. | Isopentane. | Benzene. | Isopentane. | Benzene. |
| ·002949 | ·5366 | ·5359 | ...... | ...... | ...... | ...... | ...... | ...... |
| ·005898 | ·5660 | ·5643 | ...... | ...... | ...... | ...... | ...... | ...... |
| ·011795 | ·5994 | ·5989 | ·3685 | ·3648 | ...... | ...... | ...... | ...... |
| ·022411 | ·6346 | ·6334 | ·3780 | ·3742 | 101·6 | ...... | 1·040 | ...... |
| ·044232 | ·6777 | ·6765 | ·3910 | ·3870 | 53·5 | 54·4 | 1·070 | 1·052 |
| ·088465 | ·7292 | ·7282 | ·4086 | ·4053 | 27·7 | 28·2 | 1·111 | 1·091 |
| ·14744 | ·7732 | ·7725 | ·4263 | ·4233 | 16·9 | 17·25 | 1·159 | 1·136 |
| ·20642 | ·8059 | ·8052 | ·4421 | ·4389 | 12·0 | 12·35 | 1·215 | 1·180 |
| ·29488 | ·8434 | ·8429 | ·4636 | ·4602 | 8·29 | 8·49 | 1·289 | 1·260 |
| ·44232 | ·8902 | ·8906 | ·4989 | ·4960 | 5·27 | 5·35 | 1·427 | 1·408 |
| ·58978 | ·9266 | ·9270 | ·5388 | ·5353 | 3·69 | 3·72 | 1·588 | 1·582 |
| ·73721 | ·9566 | ·9566 | ·5884 | ·5845 | 2·65 | 2·69 | 1·825 | 1·806 |
| ·82568 | ·9722 | ·9725 | ·6275 | ·6250 | 2·19 | 2·20 | 2·007 | 2·006 |
| ·88465 | ·9800 | ·9824 | ·6656 | ·6613 | 1·89 | 1·91 | 2·186 | 2·180 |
| ·94363 | ·9918 | ·9915 | ·7232 | ·7113 | 1·58 | ...... | 2·488 | ...... |
| ·97313 | ·9963 | ...... | ·7755 | ...... | 1·39 | ...... | 2·754 | ...... |
| 1·00000 | 1·0000 | 1·0000 | 1·0000 | 1·0000 | 1·00 | 1·00 | 3·73 | 3·71 |

## LIII. *The Specific Volumes of Isopentane Vapour at Low Pressures.* *By* SYDNEY YOUNG, *D.Sc., F.R.S., and* G. L. THOMAS, *B.Sc., University College, Bristol.*

DETERMINATIONS of the volumes of a gram of the unsaturated vapour of isopentane were made in a modified Hofmann's vapour-density apparatus similar in principle to that employed by Ramsay and Young (Phil. Trans. 1887, A. p. 58) in their research on ether.

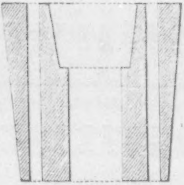
The specimen of isopentane was the same as that used by one of us in the determination of the thermal properties of the substance.

The following alterations were made in the vapour-density apparatus :—

1. A narrow tube A' (fig. 1) was sealed to the large volume tube A in order that the perforation through the indiarubber cork B might be diminished in diameter.

2. The tube was graduated throughout its entire length in millims., and the readings of both columns of mercury were taken directly on the tube, whereas formerly a graduated mirror-scale, placed behind the vapour-density tube, was employed. The direct method of reading was found to be far more convenient and was probably rather more accurate.

Fig. 2.



3. The small mercury-trough used for inserting the vapour-density tube in the apparatus was cut in the indiarubber cork as indicated in fig. 2, which represents a vertical section through the cork.

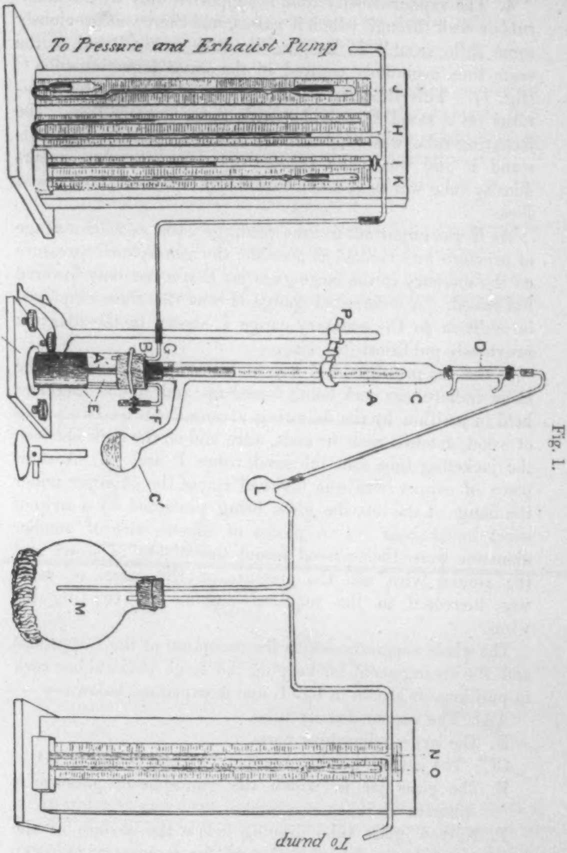


Fig. 1.

4. The vapour-density tube is supported only by the indiarubber cork through which it passes, and there was previously some little trouble in keeping the tube vertical, and at the same time accurately centred in the outer jacketing-tube C (fig. 1). This difficulty was overcome by placing the apparatus on a stand Q provided with three screwed feet. The jacketing-tube was supported by a clamp and large retort-stand P and was made vertical once for all; the vapour-density tube was then easily centred by means of the screwed feet.

As it was important to take readings over as wide a range of pressure and volume as possible, the atmospheric pressure on the mercury in the large glass jar E was not only lowered but raised. A differential gauge H was therefore employed in addition to the ordinary gauge I, shown in the diagram previously published (*loc. cit.*).

When the pressure in E was high there was danger of the large indiarubber cork being forced up, and it was therefore held in position by the following arrangement:—Two pieces of wood, notched near the ends, were laid on the cork between the jacketing tube and the small tubes F and G. A stout piece of copper wire was fastened round the glass jar under the flange at the top, the glass being protected by a strip of sheet indiarubber. Two pieces of copper wire of smaller diameter were then passed round the pieces of wood and the stouter wire, and the pressure on the pieces of wood was increased to the required amount by twisting the wires.

The whole apparatus—with the exception of the two pumps and the arrangement for keeping the large indiarubber cork in position—is shown in fig. 1, and is explained below:—

AA′. The vapour-density tube.

B. The large indiarubber cork.

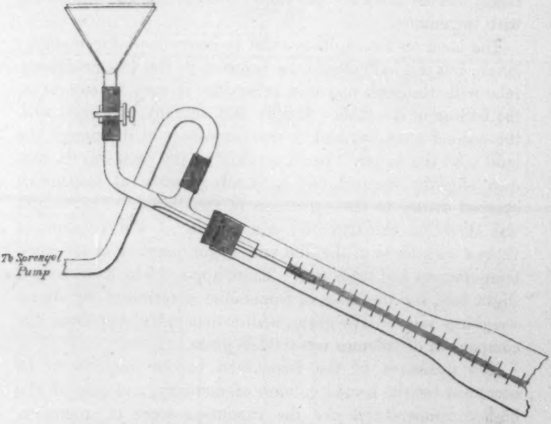
CC′. The jacketing-tube provided with the condenser D.

E. The glass jar in which the atmospheric pressure is altered.

F. Narrow glass tube dipping below the surface of the mercury in the jar and used for removal of mercury after insertion of the vapour-density tube.

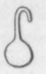
G. Narrow glass tube passing just through the indiarubber cork and connected by lead or glass tubing with
HI the differential and ordinary gauges.
JK. Barometers.
L. Small bulb to collect any of the jacketing substance not condensed at D. It occasionally happens that a little carbon bisulphide or alcohol, when boiling under reduced pressure, escapes condensation at D.
M. A large air-reservoir to prevent oscillation of the mercury columns in the gauge N.
NO. Gauge and barometer for measuring the pressure under which the liquid in the bulb C′ is boiling.
P. Retort-stand and clamp to support the jacketing-tube.
Q. Wooden stand with three screws to centre the vapour-density tube.

Fig. 3.



In order to avoid the presence of air in the vapour-density tube it was filled with mercury in the manner indicated in the diagram (fig. 3). The tube was thoroughly exhausted by means of a Sprengel pump, and was heated to remove the film of air adhering to the glass. Filtered mercury was then run slowly into the tube, the Sprengel pump being kept constantly in action and the tube hot until it was nearly filled*. After cooling, the vapour-density tube was removed, a little more mercury added so as to completely fill it, and it was then inverted in a large trough of mercury. The isopentane was weighed in a small bulb (fig. 4) provided with a hooked capillary neck, and the bulb was passed up into the tube immediately after being weighed.

Fig. 4.



The evaporation from the capillary tube is extremely slow if the temperature is sufficiently below the boiling-point of the liquid, but with such a volatile substance as isopentane it is advisable to choose a cool day. That no sensible loss by evaporation was taking place was proved by the fact that the difference of reading for 1 mgrm. (by the method of oscillations) was the same for the empty bulb as for the bulb filled with isopentane.

The hook on the capillary tube is convenient for manipulation, but the bulb should be inserted in the vapour-density tube with the hook upwards, otherwise it may be caught at the bottom of the tube. This, in fact, actually happened with the second quantity, and it was necessary to disengage the bulb with the finger. In all probability the bulb was in this case slightly warmed and a small quantity of isopentane escaped owing to the expansion of the liquid. The weight was therefore calculated by comparison of the volumes of vapour with those of the first and larger quantity at the same temperatures and pressures. There appeared to have been a slight loss, for the mass of isopentane determined by direct weighing was 0·0376 gram, whilst that calculated from the comparison of volumes was 0·0373 gram.

The pressures of the isopentane vapour require to be corrected for the heated column of mercury, and also at the higher temperatures for the vapour-pressure of mercury. The first correction is necessarily uncertain, as it is impossible to decide exactly how far down the tube the mercury is heated. It was assumed that its temperature was that of the jacketing vapour down to 1 centim. below the surface of the condensed liquid in the jacketing-tube. The error involved is extremely small at the lower temperatures, but increases with rise of temperature. The readings with the larger quantity of substance were therefore taken only to 150° and with the smaller quantity to 100°.

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* All the indiarubber tubes and corks with which the mercury could come in contact had been boiled with strong potash.

The data obtained are given in the following table; the mass of the larger quantity of isopentane, obtained by direct weighing, was 0·1290 gram, that of the smaller quantity was 0·0373 gram. The value of $\frac{PV}{T}$, taking the molecular weight of isopentane as 71·85 and the weight of a litre of hydrogen at 0° and 760 millim. as 0·0899 gram, would be 862.

Series I.

| Temp. | Pressure. millims. | Volume. cub. cms. | $\frac{PV}{T}$. |
|---|---|---|---|
| 10°·75 | 190·8 | 1273·0 | 856·1 |
| | 206·8 | 1169·5 | 852·7 |
| | 226·5 | 1066·5 | 851·4 |
| | 250·6 | 962·3 | 850·0 |
| | 279·6 | 861·5 | 849·0 |
| | 318·7 | 753·3 | 846·2 |
| | 359·1 | 666·5 | 843·7 |
| | 390·9 | 610·8 | 841·7 |
| 30° ... | 211·1 | 1230·5 | 857·2 |
| | 228·2 | 1133·5 | 853·9 |
| | 250·7 | 1032·5 | 854·1 |
| | 278·3 | 928·2 | 852·6 |
| | 291·1 | 886·3 | 851·5 |
| | 326·8 | 787·8 | 849·7 |
| | 375 1 | 684·2 | 847·0 |
| | 437·6 | 584·3 | 843·9 |
| | 530·0 | 479·7 | 839·0 |
| | 654·5 | 385·5 | 832·7 |
| | 755·2 | 331·6 | 826·4 |
| 40° ... | 219·1 | 1224·0 | 856·8 |
| | 239·3 | 1118·5 | 855·0 |
| | 263·5 | 1014·5 | 854·0 |
| | 291·0 | 916·8 | 852·4 |
| | 330·4 | 805·7 | 850·5 |
| | 378·7 | 701·9 | 849·2 |
| 40° ... (*cont.*) | 443·2 | 597·1 | 845·5 |
| | 517·9 | 508·6 | 841·5 |
| | 610·4 | 429·2 | 837·0 |
| | 757·7 | 343·1 | 830·5 |
| 50° ... | 219·7 | 1257·0 | 855·1 |
| | 239·2 | 1153·5 | 854·2 |
| | 262·6 | 1050·0 | 853·7 |
| | 293·8 | 935·7 | 852·7 |
| | 327·2 | 841·0 | 851·9 |
| | 372·8 | 736·6 | 850·2 |
| | 432·0 | 632·3 | 845·6 |
| | 510·6 | 533·7 | 843·7 |
| | 607·2 | 446·2 | 838·9 |
| | 733·8 | 367·1 | 834·1 |
| 60° ... | 233·4 | 1222·5 | 856·9 |
| | 254·7 | 1119·0 | 856·1 |
| | 280·3 | 1015·5 | 854·6 |
| | 312·6 | 909·7 | 854·0 |
| | 351·9 | 806·8 | 852·6 |
| | 402·3 | 702·9 | 849·2 |
| | 471·7 | 597·9 | 847·0 |
| | 567·9 | 494·9 | 844·0 |
| | 683·9 | 408·7 | 839·4 |
| | 790·2 | 351·8 | 834·8 |

Series I. (*continued*).

| Temp. | Pressure millims. | Volume. cub. cms. | $\frac{PV}{T}$. |
|---|---|---|---|
| 70° ... | 240·8 | 1222·0 | 857·8 |
| | 262·1 | 1119·0 | 855·2 |
| | 288·8 | 1015·0 | 854·8 |
| | 318·8 | 919·5 | 854·6 |
| | 355·0 | 824·1 | 853·0 |
| | 405·3 | 720·1 | 850·9 |
| | 472·0 | 616·0 | 847·7 |
| | 565·7 | 512·4 | 845·1 |
| | 675·8 | 427·0 | 841·2 |
| | 789·2 | 363·7 | 836·8 |
| 80° ... | 247·2 | 1222·0 | 855·8 |
| | 269·9 | 1119·5 | 855·8 |
| | 297·3 | 1015·5 | 855·3 |
| | 325·6 | 927·2 | 855·2 |
| | 365·3 | 823·9 | 852·6 |
| | 417·1 | 720·2 | 850·9 |
| | 486·4 | 616·1 | 849·0 |
| | 564·0 | 529·9 | 846·7 |
| | 669·3 | 444·5 | 842·8 |
| | 798·2 | 370·8 | 838·5 |
| 90° ... | 254·4 | 1222·5 | 856·9 |
| | 277·5 | 1119·5 | 855·8 |
| | 305·7 | 1016·0 | 855·5 |
| | 334·9 | 926·9 | 855·2 |
| | 375·6 | 824·3 | 852·9 |
| | 429·2 | 720·2 | 851·5 |
| | 500·8 | 615·6 | 849·3 |
| | 580·1 | 530·1 | 847·1 |
| | 689·5 | 444·6 | 844·5 |
| | 815·6 | 374·0 | 840·4 |
| 100°... | 261·3 | 1223·5 | 857·0 |
| | 285·3 | 1120·0 | 856·8 |
| | 314·1 | 1016·0 | 855·6 |
| | 341·2 | 935·2 | 855·5 |
| | 386·2 | 824·8 | 853·9 |
| | 441·5 | 720·0 | 852·2 |
| | 501·3 | 633·3 | 851·1 |
| | 578·4 | 547·5 | 849 0 |
| | 684·0 | 461·9 | 847·0 |
| | 825·1 | 380·5 | 841·7 |
| 110°... | 268·6 | 1224·5 | 858·7 |
| | 293·2 | 1120·5 | 857·8 |
| | 317·5 | 1034·0 | 857·0 |
| | 350·6 | 935·6 | 856·4 |
| | 397·4 | 824·7 | 855·7 |
| | 454·2 | 720·2 | 854·0 |
| 110°... (*cont.*) | 514·9 | 633·4 | 851·5 |
| | 593·2 | 549·7 | 851·4 |
| | 698·1 | 465·5 | 848·5 |
| | 849·6 | 380·4 | 843·9 |
| 120°... | 275·2 | 1224·5 | 857·4 |
| | 300·6 | 1120·5 | 857·2 |
| | 325·7 | 1034·1 | 857·0 |
| | 356·4 | 945·1 | 857·1 |
| | 391·4 | 859·5 | 856·0 |
| | 435·7 | 772·1 | 856·2 |
| | 489·3 | 685·5 | 853·5 |
| | 558·3 | 600·4 | 853·3 |
| | 653·0 | 512·9 | 852·2 |
| | 753·1 | 442·5 | 848·0 |
| | 868 6 | 382·8 | 846·1 |
| 130°... | 282·2 | 1224·5 | 857·5 |
| | 303·7 | 1138·5 | 857·8 |
| | 328·8 | 1051·5 | 857·9 |
| | 362·4 | 954·0 | 857·9 |
| | 393·2 | 877·0 | 856·3 |
| | 435·9 | 791·8 | 856·5 |
| | 490·3 | 703·5 | 855·9 |
| | 558·3 | 616·5 | 854·0 |
| | 646·3 | 531·1 | 851·8 |
| | 746·0 | 459·7 | 850·9 |
| | 872·1 | 391·6 | 847·4 |
| 140°... | 293·7 | 1206·5 | 858·1 |
| | 311·5 | 1138·5 | 858·7 |
| | 336·9 | 1023·0 | 857·9 |
| | 367·1 | 966·4 | 859·0 |
| | 404·2 | 877·2 | 858·5 |
| | 447·9 | 790·5 | 857·3 |
| | 502·6 | 703·8 | 856·5 |
| | 571·2 | 618·5 | 855·4 |
| | 663·6 | 531·3 | 853·7 |
| | 762·9 | 461·0 | 851·6 |
| | 899·1 | 390·0 | 849·0 |
| 150°... | 300·4 | 1208·5 | 858·2 |
| | 319·3 | 1138·0 | 859·0 |
| | 345·4 | 1052·5 | 859·2 |
| | 371·7 | 977·4 | 858·9 |
| | 413·4 | 877·4 | 859·5 |
| | 459·7 | 790·6 | 859·1 |
| | 513·8 | 705·9 | 857·4 |
| | 586·9 | 618·1 | 857·6 |
| | 682·3 | 530·4 | 855·6 |
| | 783·8 | 460·3 | 852 9 |
| | 912·5 | 394·2 | 850·4 |

## Series II.

| Temp. | Pressure. millims. | Volume. cub. cms. | $\frac{PV}{T}$. |
|---|---|---|---|
| 11°·0 | 60·7 | 4045 | 864 |
| | 66·6 | 3685 | 864 |
| | 73·6 | 3326 | 862 |
| | 82·8 | 2965 | 865 |
| | 93·7 | 2606 | 860 |
| | 108·6 | 2246 | 859 |
| | 129·0 | 1888 | 857 |
| | 158·9 | 1529 | 856 |
| | 205·7 | 1176 | 852 |
| | 287·5 | 837 | 847 |
| 16°·3 | 61·8 | 4044 | 864 |
| | 67·8 | 3686 | 864 |
| | 75·2 | 3324 | 864 |
| | 84·0 | 2965 | 861 |
| | 95·5 | 2607 | 860 |
| | 110·7 | 2245 | 859 |
| | 131·7 | 1883 | 857 |
| | 163·4 | 1516 | 856 |
| | 209·5 | 1178 | 853 |
| | 298·3 | 821 | 847 |
| | 451·8 | 536 | 837 |
| 30°... | 64·6 | 4047 | 863 |
| | 70·8 | 3691 | 862 |
| | 78·9 | 3331 | 867 |
| | 88·0 | 2968 | 862 |
| | 100·5 | 2602 | 863 |
| | 116·0 | 2249 | 861 |
| | 138·2 | 1882 | 859 |
| | 170·1 | 1526 | 857 |
| | 221·0 | 1171 | 854 |
| | 257·2 | 1006 | 854 |
| | 315·2 | 816 | 849 |
| 40°... | 66·8 | 4048 | 864 |
| | 73·4 | 3688 | 865 |
| | 81·6 | 3325 | 867 |
| | 91·3 | 2969 | 866 |
| | 103·8 | 2606 | 864 |
| | 120·0 | 2245 | 861 |
| | 142·7 | 1888 | 861 |
| | 175·5 | 1528 | 857 |
| | 228·3 | 1172 | 854 |
| | 266·6 | 1000 | 852 |
| | 322·7 | 823 | 849 |
| 50°... | 69·0 | 4050 | 865 |
| | 75·6 | 3694 | 865 |
| | 84·1 | 3335 | 866 |
| | 93·9 | 2970 | 864 |
| | 107·1 | 2602 | 863 |
| | 123·8 | 2247 | 861 |
| | 146·8 | 1895 | 861 |
| | 180·4 | 1537 | 858 |
| | 235·7 | 1171 | 855 |
| | 276·1 | 999 | 854 |
| | 333·4 | 825 | 851 |
| 60°... | 70·8 | 4044 | 860 |
| | 77·8 | 3697 | 864 |
| | 86·5 | 3336 | 867 |
| | 96·9 | 2968 | 864 |
| | 109·9 | 2607 | 861 |
| | 127·3 | 2253 | 861 |
| | 151·2 | 1892 | 859 |
| | 187·5 | 1525 | 858 |
| | 242·9 | 1171 | 858 |
| | 285·5 | 995 | 853 |
| | 349·0 | 812 | 851 |
| 70°... | 73·4 | 4046 | 866 |
| | 80·6 | 3687 | 866 |
| | 89·1 | 3331 | 865 |
| | 99·8 | 2971 | 864 |
| | 113·5 | 2608 | 863 |
| | 131·4 | 2249 | 862 |
| | 155·6 | 1894 | 859 |
| | 192·2 | 1531 | 858 |
| | 249·0 | 1177 | 855 |
| | 292·1 | 1004 | 855 |
| | 356·6 | 1817 | 850 |
| 80°... | 75·5 | 4042 | 865 |
| | 82·6 | 3694 | 864 |
| | 91·8 | 3338 | 868 |
| | 103·0 | 2968 | 866 |
| | 116·6 | 2614 | 864 |
| | 134·8 | 2254 | 861 |
| | 160·5 | 1889 | 859 |
| | 196·7 | 1543 | 860 |
| | 257·7 | 1172 | 856 |
| | 304·6 | 991 | 855 |
| | 364·8 | 824 | 851 |
| 90°... | 77·4 | 4053 | 864 |
| | 85·1 | 3696 | 867 |
| | 94·6 | 3329 | 868 |
| | 106·0 | 2976 | 869 |
| | 120·4 | 2605 | 864 |
| | 139·2 | 2248 | 862 |
| | 165·7 | 1888 | 862 |
| | 203·0 | 1540 | 861 |
| | 266·6 | 1170 | 859 |
| | 312·8 | 994 | 857 |
| | 378·9 | 818 | 854 |
| 100°... | 79·4 | 4048 | 862 |
| | 87·4 | 3692 | 865 |
| | 97·2 | 3340 | 870 |
| | 109·1 | 2967 | 868 |
| | 123·8 | 2610 | 866 |
| | 142·6 | 2257 | 863 |
| | 170·9 | 1884 | 863 |
| | 208·9 | 1539 | 862 |
| | 271·6 | 1180 | 859 |
| | 321·5 | 995 | 858 |
| | 392·6 | 813 | 855 |

## LIV. *Isopentane from Amyl Iodide.* *By* SYDNEY YOUNG, *D.Sc., F.R.S., and* G. L. THOMAS, *B.Sc., University College, Bristol.*

ISOPENTANE has been prepared from amyl iodide by Frankland (Trans. Chem. Soc. iii. pp. 31 and 481) by the action of zinc and water, and by Just (*Annalen*, ccxx. p. 146) by the action of zinc and hydrochloric acid.

Frankland gives the boiling-point of his specimen of isopentane as 30° under a pressure of 734 millim., and Just as 30° under the normal pressure. These boiling-points are considerably higher than that of the isopentane employed in the researches described in the accompanying papers.

The specific gravities observed by Frankland and by Just are also much higher than any others recorded. On the other hand, Mr. J. W. Rodger informs us that he has prepared specimens of isopentane from amyl iodide made from Scotch and Irish amyl alcohol, and that the boiling-point in each case was almost exactly 28°.

As it was of importance to obtain every possible proof of the purity of the isopentane employed for the determination of the physical constants of that substance, we thought it advisable to compare its properties with those of a specimen prepared from amyl iodide. The iodide was obtained from Burgoyne & Co.; it boiled within moderate limits of temperature, and it was not thought necessary to fractionate it.

The replacement of the iodine by hydrogen was effected in two different ways:—(*a*) by the action of the zinc-copper couple on a strong alcoholic solution; (*b*) by the slow addition of very strong hydrochloric acid to amyl iodide, dissolved in a large quantity of alcohol, in presence of zinc slightly covered with copper.

In the first case zinc-foil was employed, and the couple was prepared by the method recommended by Gladstone and Tribe (Trans. Chem. Soc. xlv. p. 154); it was thoroughly washed with water, and finally twice with alcohol. The amyl iodide, dissolved in rather more than its own volume of absolute alcohol, was added and then a few drops of hydrochloric acid. The flask containing the mixture was provided with a reversed condenser and a glass tube, bent twice at right angles, the end of which dipped under mercury.

The action at the temperature of the room (about 10°) was slow, for after forty hours, when a few drops of the liquid were added to water, the oil which separated sank to the bottom. Some isopentane, however, had been formed, and it was distilled off and collected. The remainder of the alcoholic solution of amyl iodide was then subjected to the action of the zinc-copper couple for twenty hours at a temperature of from 30° to 35°. The alcoholic solution of isopentane was then distilled from the flask containing the couple, and the distillate was shaken several times with water to remove alcohol. A considerable amount of amylene was present, and bromine was therefore added until the isopentane remained permanently coloured. The excess of bromine was removed with caustic soda, and the isopentane was washed with water, dried with calcium chloride, and distilled. The temperature rose from 27°·5 to about 50°, when the distillation was stopped, a considerable amount of amylene dibromide being left in the flask. The quantity of crude isopentane was too small to allow of satisfactory fractionation, and it was therefore mixed with the substance obtained by the other method.

The remainder of the amyl iodide was treated by the method described by Just (*loc. cit.*) except that the zinc, after purification with dilute acid, was treated once with a 2-per-cent. solution of copper sulphate. The action was evidently greatly accelerated by the presence of the copper, for Just states that the conversion was not complete until after 9 or 10 days, whereas we found that very little iodide was left after less than 24 hours.

The amyl iodide, dissolved in five times its volume of absolute alcohol, was added to the zinc-copper couple in a flask cooled by ice, and the hydrochloric acid (obtained by saturating the pure concentrated acid, cooled by water,.with the gas) was added drop by drop from a separating funnel. A reversed condenser was, of course, unnecessary, as the temperature was maintained at 0°, but the flask was provided with a glass tube bent twice at right angles and dipping under mercury. It was found that the evolution of hydrogen was not great until the reduction of the iodide was nearly complete.

After about 24 hours it was found that when a few drops of the alcoholic solution were added to water, a light liquid separated and floated on the water. The solution was then poured away from the zinc and was distilled from the water-bath until, on addition of a small quantity of the distillate to water, no further separation of isopentane took place.

The distillate was shaken several times with water to remove alcohol, and was treated in the same manner as the isopentane obtained by the other method. In this case, however, it was found that the amount of bromine required to remove the amylene was very much smaller, and also that the yield of isopentane was better.

The two quantities of isopentane were mixed together and, after being distilled from phosphorus pentoxide, were fractionated eight times from a distillation-bulb with a long still-head. A fair quantity of substance, boiling quite constantly at 27°·6 under a pressure of 750·6 millim., was obtained.

The isopentane was subsequently distilled on four occasions from phosphorus pentoxide, and the observed boiling-points are given below:—

| Pressure. | Temperature. | Corrected to 760 millim. |
|---|---|---|
| 750·6 | 27·6 | 27·95 |
| 753·2 | 27·7 | 27·95 |
| 751·8 | 27·65 | 27·95 |
| 768·0 | 28·2 | 27·9 |
| | Mean . . . . | 27·95 |

The mean boiling-point is identical with that of the specimen prepared from Kahlbaum's "pentane." The specific gravity was determined at 0° and 13°·4 in the modified Sprengel tube, with the following results :—

Sp. gr. at 0°... 0·63935 ; at 13°·4... 0·62632.

The mean specific gravity at 0° of the other sample was 0·63924.

The vapour-pressures and the volumes of a gram of liquid and saturated vapour were determined at three temperatures, and a few volumes and pressures also at the critical temperature. The results are given in the following table and, for the sake of comparison, those obtained under similar conditions with the other specimen of isopentane are added.

It will be seen that the agreement is satisfactory, and additional evidence is thus afforded of the purity of the substance.

The observed critical temperature was 187°·8 (the substance being heated with aniline vapour under increased pressure). This is identical with the mean temperature observed with the sample from Kahlbaum's "pentane."

Vapour Pressure.

| Temperature. | *Isopentane from Amyl Iodide.* | *"Pentane" from Kahlbaum.* |
|---|---|---|
| 160° | 16316 | 16323 |
| 170° | 19117 | 19115 |
| 180° | 22270 | 22270 |

Volumes of a Gram.

| | *Isopentane from Amyl Iodide.* | | *"Pentane" from Kahlbaum.* | |
|---|---|---|---|---|
| | Liquid. | Saturated Vapour. | Liquid. | Saturated Vapour. |
| 160° | 2·3745 | 13·70 | 2·3775 | 13·71 |
| 170° | 2·5545 | 10·73 | 2·5550 | 10·73 |
| 180° | 2·8560 | 7·943 | 2·8590 | 7·952 |

Critical Isothermal.

| | Volume. | Pressure. | |
|---|---|---|---|
| | | *Isopentane from Amyl Iodide.* | *"Pentane" from Kahlbaum.* |
| 187°·8 | 3·067 | 26060 | 26040 |
| | 3·268 | 25350 | 25310 |
| | 3·468 | 25120 | 25070 |
| | 3·871 | 25040 | 25030 |
| | 4·276 | 25020 | 25010 |
| | 4·679 | 25040 | 25000 |
| | 5·086 | 25020 | 24990 |
| | 5·493 | 24980 | 24960 |
| | 5·902 | 24880 | 24870 |
| | 6·306 | 24740 | 24730 |

## LV. *The Gladstone "Law" in Physical Optics, and the True Volume of Liquid Matter.* By WALTER HIBBERT, *F.I.C.*

ONE of the curious results established in Chemical Optics is that two independent formulæ (those of Gladstone and Lorentz respectively) can be used in the discussion of experimental data relating to the refractive index and the density of a given substance. Neither of them can claim any special advantage. They both have a wide range of application, yet neither holds universally good. Still more curiously, they break down under quite different conditions of experiment.

The Lorentz formula,

$$\frac{\mu^2-1}{\mu^2+2}\cdot\frac{1}{d}=\text{constant},$$

which is able to cover the large variation in density separating a liquid and its vapour, gives erroneous results in the simple case of a liquid whose density is changed by pressure. On the other hand, the Gladstone formula,

$$\frac{\mu-1}{d}=\text{constant},$$

is unique in its power to deal with liquids under varying pressure, but fails in the jump from liquid to vapour.

Hitherto no light has been thrown on these anomalies, but this present paper attempts to explain the exceptions in the case of the Gladstone expression, and, incidentally, introduces a physical magnitude which is conveniently described as the "actual volume occupied by one gramme of the substance."

The suggestion of the present argument arose out of a number of experiments carried out by Dr. Gladstone and myself during the last two years. We have examined a great variety of salt-solutions, whose strength varied from saturation down to about 5 per cent.—a dilution limit imposed by experimental error when the hollow-prism method is adopted for obtaining the refractive index.

Our main conclusion, to the effect that the value of $\frac{\mu-1}{d}$ for the salt is practically constant, has received special confirmation by the publication of a paper by Kohlrausch and Hallwachs[*], in which they extend the work on about 10 salts to extremely dilute solutions. They used an interference method for determining $\mu$, and a special apparatus for getting $d$ with the necessary accuracy, so that the experimental error is not larger than usual, even when the amount of salt present is not greater than 0·05 per cent. of the solution.

An examination of this body of evidence proved to me that the constancy of $\mu-1/d$ was much greater for an ordinary dissolved salt than for a simple liquid whose density is changed by heat. For example:—

When heptane is heated from 12° to 88° its density changes by about 10 per cent., and the value of $\mu-1/d$ by 0·55 per cent.

Sodium chloride, diluted from 13 per cent. down to 0·03 per cent. (a concentration change of 400 to 1), has its value for $\mu-1/d$ changed by 0·22 per cent. only.

In speculating on this far greater constancy in the case of a dissolved salt, it seemed not unreasonable to regard the solution in the light of Van't Hoff's theory, attributing a pseudo-gaseous condition to the dissolved salt. This at once suggested other comparisons, and led to the following summary statement of all experimental results on the subject:—

1. The Gladstone expression is true in the case of gases whose density is changed by varying pressure[†].
2. It is true in the case of liquids whose density is changed by varying pressure[‡].
3. It is true (or a *very* close approximation) in the case of dissolved salts, especially in dilute solution.
4. It is a less close approximation in the case of simple liquids undergoing thermal expansion.
5. It altogether fails when a liquid is changed into vapour.

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[*] Wied. *Ann.* 1894, liii. p. 1.

[†] Biot and Arago, *Mém. d. l'Inst.* vii. p. 301 (1806), and Chappuis and Rivière, *Compt. Rend.* ciii. Biot and Arago express their results $(\mu^2-1)v=\text{const.}$ But $\mu^2$ is only slightly greater than unity, and therefore $(\mu-1)v$ must also be constant.

[‡] Quincke, Phil. Mag. 1884, xvii. p. 65.

On studying the results included in 4, it appeared that they had one point in common. If the variation be expressed in symbols, it may be put in the form

$$e_t = e_0(1 \pm at),$$

where $e_0$ and $e_t$ are the values of $\frac{\mu-1}{d}$ at 0° and $t$° respectively. Examination showed that all good experiments gave a negative sign for the coefficient $a$. In other words, the value of $e$ always diminishes as the density diminishes. If we put $(\mu-1)/d=(\mu-1)v$, where $v$ is the volume of unit mass, we may say that $(\mu-1)v$ always diminishes as $v$ increases. This statement is still more emphatically true when the liquid becomes a vapour.

Therefore, in classes 4 and 5, whenever $v$ increases the product $(\mu-1)v$ diminishes. In liquids, where the change in $v$ is not very great, the diminution of the product is small; but in passing to vapour, where the change in $v$ is enormous, the product $(\mu-1)v$ undergoes a large diminution. To put the same thing in the inverse sense, the results show that when $v$ becomes comparatively small, there is a marked increase in the product. So stated, they afford criteria by which we may possibly find the cause of the deficiency. The conditions are almost a reproduction of those which led to the second approximation in the case of Boyle's law. Experiment showed that the product $pv$ was only constant when $v$ was comparatively large. As $v$ diminished, there was a tendency for the product to increase, and it became necessary to suppose that the expression $pv$ referred not to the whole space symbolized by $v$, but to $v$ minus the space occupied by the particles. Hence $p(v-b)$, where $b$ is the actual volume of the matter, has taken the place of $pv$.

It appeared to me, that the similar experimental results would warrant the introduction of a similar symbol in the Gladstone expression, thus transforming it into

$$(\mu-1)(v-\beta) = \text{constant}.$$

It is at once apparent that the introduction of $\beta$ tends to remove the anomalies, and also evident why cases 1, 2, and 3 in the above summary are satisfied by the uncorrected formulæ.

In 1 and 3, that is in the case of gases and dissolved salts respectively, the value $\beta$ is negligible compared with $v$.

In 2, owing to the very slight compressibility of the liquids, the changes in $v$ are always exceedingly small. Hence $v-\beta$ will change almost as much as $v$, if, as is probable, $\beta$ is not a large fraction of $v$.

In 4, the case of liquids undergoing thermal expansion, the changes in $v$ are great enough, as compared with the value of $\beta$, to cause an appreciable difference between the ratios $v/v_1$ and $(v-\beta)/(v_1-\beta)$.

In 5, the case of vaporization, we have $v$ for the liquid comparatively small, changing into a very large value in the vapour. Here there is a decided and altogether disturbing difference between the ratios $v/v_1$ and $(v-\beta)/(v_1-\beta)$*.

Evidently, then, if the numerical data are found to be of the right order, the introduction of $\beta$ will remove the reservations with which the Gladstone law is usually stated. Moreover, the physical conditions under which $\beta$ needs to be introduced render it probable that $\beta$ has, or may have, a physical meaning, and is not merely of the nature of an arbitrary constant. But the real justification for introducing $\beta$ must be, *à posteriori*, by showing that the calculated values are not improbable, and that they have relations to other physical quantities.

We can determine $\beta$ for any one substance from observations on a liquid at two different temperatures.

Let $\mu_1$, $\mu_2$ be the refractive indices ; $v_1$, $v_2$ the volumes of unit mass $\left(=\frac{1}{d}\right)$ at the temperatures of two experiments, and let $\beta$ have the meaning suggested, then

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* This paper was written out before I recalled the fact that Ketteler suggested the same solution for the discrepancies experienced in applying the expression $(\mu^2-1)v=\text{constant}$. Writing it $(\mu^2-1)(v-\beta)$ he examined a series of experiments made by Weegmann (*Zeit. phys. Chem.* ii. p. 905). The result was not very encouraging. But I am of opinion that there are two reasons for that discouragement. First, Weegmann happened to work on substances of exceptional density, a fact which ought to foreshadow the probability of exceptional results in any volume deduced from them. Secondly, the expression $(\mu^2-1)v$ is surely not so good a basis for the investigation as the simpler one due to Gladstone and Dale. In ordinary liquids it is not so constant; it is not supported by Quincke's experiments on liquids under pressure (*comp.* Sutherland, Phil. Mag. 1888); nor does it render such service in Physical Chemistry as either the Gladstone or Lorentz expression.

$$(\mu_1-1)(v_1-\beta)=(\mu_2-1)(v_2-\beta),$$

and

$$\beta=\frac{(\mu_1-1)v_1-(\mu_2-1)v_2}{\mu_1-\mu_2}.$$

This equation shows that the measure of $\beta$ will depend on differences which we know to be small, and it is at once evident that the best experiments only will be serviceable. Thus, a table of results for carbon disulphide gives the following figures for the temperatures of 0° and 40° Centigrade; the data are Ketteler's:—

$$\mu_1=1{\cdot}64375,\ \mu_2=1{\cdot}61187\ ;\ v_1={\cdot}77314,\ v_2={\cdot}81103.$$

Therefore

$$\beta=\frac{0{\cdot}497709-0{\cdot}496245}{0{\cdot}03188}=\frac{0{\cdot}001464}{0{\cdot}03188}=0{\cdot}0459.$$

Here the difference between the two terms of the numerator is only $\frac{1}{350}$ of either, and as each term involves only the fractional part of the index, any error in $\mu$ is multiplied about 900 times in its effect on $\beta$.

This makes it imperative to attach weight only to those experiments where special appliances have been adopted to keep the temperature constant during the observations. For this reason I simply allude to the few results I have myself obtained in a few preliminary experiments, reserving data for a fuller discussion. The results here presented depend almost entirely on the work of three sets of observers, namely, Nasini and Bernheimer, Perkin, and Ketteler. It would be invidious for me to single out one of these as more accurate than the others; their papers show that all the experiments are of a high order of accuracy. It is doubtful, however, whether Perkin's data are not the most serviceable for our present purpose, if only for the reason that the interval of temperature he employed is greater, with the consequence that the differences on which $\beta$ depends become more marked, and thereby afford greater accuracy.

Table I. is drawn up from a paper by Nasini and Bernheimer*. They were the first to use a jacketed prism, so that their results are the earliest of those suitable for deducing $\beta$. One substance in their list—bromonaphthalene—has been omitted, as it stands alone in giving an increase in $(\mu-1)v$ on heating. It is probable that the limit of experimental error is reached with that substance.

Table I.

| Substance. | Temp. | Density. | $\mu_\alpha$. | $\beta = \frac{(\mu-1)v-(\mu_1-1)v_1}{\mu-\mu_1}$. | $v$ at lower temp. | $\frac{\beta}{v}$. |
|---|---|---|---|---|---|---|
| Thymol, $C_{10}H_{14}O$. | 24° | 0·96895 | α1·51453 | 0·0563 | | |
| | 77·3 | 0·92838 | α1·49189 | 0·0600 | | |
| | | | | 0·0623 | | |
| | | | | Mean 0·0600 | 1·0320 | 0·058 |
| Cinnamic Alcohol, $C_9H_{10}O$. | 24·8 | 1·04017 | 1·57311 | 0·077 | | |
| | 77·3 | 1·00027 | 1·54939 | 0·086 | | |
| | | | | 0·011 | | |
| | | | | 0·080 | 0·96055 | 0·083 |
| Anethol, $C_{10}H_{12}O$. | 14·9 | 0·99132 | 1·55559 | 0·066 | | |
| | 77 | 0·94041 | 1·52526 | 0·063 | | |
| | | | | 0·069 | | |
| | | | | 0·066 | 1·0087 | 0·0655 |
| α-Methyl α-Naphthol, $C_{11}H_{10}O$. | 14 | 1·09636 | 1·61474 | 0·0566 | | |
| | 77 | 1·04661 | 1·58508 | 0·0570 | | |
| | | | | 0·0850 | | |
| | | | | 0·0620 | 0·9121 | 0·0680 |
| Dimethylnaphthalene, $C_{12}H_{12}$. | 16·4 | 1·01803 | 1·60765 | 0·0869 | | |
| | 77 | 0·97411 | 1·57901 | 0·0899 | | |
| | | | | 0·0893 | | |
| | | | | 0·0890 | 0·9823 | 0·09 |

Column 2 gives the temperatures, 3 the densities, and 4 the indices for the line α. Col. 5 gives three values of $\beta$ as calculated from the two indices for each of the lines α, D, and $\beta$. The indices for D and $\beta$ will be found in the original paper.

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[*] *Gaz. Chim. Ital.* xv., 1885.

The third value (that given by H$\beta$) for cinnamic alcohol appears to be wrong, and the third value for methyl $\alpha$-naphthol also, though to a less degree. In calculating the means, I have ignored the first and allowed only half weight to the second of these.

The next table contains all the observations made by Perkin*, whose apparatus was still more perfect than that of Nasini and Bernheimer. The index is quoted here for the line D only, but the quantity $\beta$ has been calculated from the lines A, C, D, and F. Where a fifth value is given, it is calculated from the line G.

Tables I. and II. contain the results yielded by substances of very varied chemical types. It may be stated at once that, although the last six substances have been put in the Table, the discussion of the figures they yield will be deferred. It is known that they are of very exceptional character; for example, that they change in chemical constitution when heated, so that it is not strictly the same substance we are dealing with at the two temperatures given in the Table†. Excluding these compounds, the values of $\beta$ are of a satisfactory order. They do not vary largely, the extreme values being 0·09 and 0·043, most of them lying between 0·065 and 0·045. That is to say, on the hypothesis which led to the calculation, the actual space filled by one gramme of the substance is about one twentieth of a cubic centimetre.

Column 7 shows the value of $\beta/v$, that is the ratio of the actual to the apparent volume of a liquid. The extremes are 0·15 and 0·054. If we exclude methylene di-iodide, a substance of exceptional density, the extremes are 0·09 and 0·054, and twelve out of the sixteen liquids lie between 0·076 and 0·054; the average value is 0·064.

These results are promising, both with regard to the absolute magnitude and the approach to similarity of value for the different liquids. This last fact was to be expected, for it is probable that ordinary liquids, under similar conditions of temperature and pressure, have volume constitutions of a fairly uniform type.

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* Chem. Soc. Journ. 1892, pp. 287 & 800.

† Compare Perkin, Chem. Soc. Journ. 1892, p. 840.

## Table II.

| Substance. | Temp | Density. | $\mu_D$. | $\beta = \dfrac{(\mu-1)v-(\mu_1-1)v_1}{\mu-\mu_1}$ | $v$ at lower temp. | $\dfrac{\beta}{v}$. |
|---|---|---|---|---|---|---|
| Heptane, $C_7H_{16}$ ...... | 12°·2<br>88·8 | 0·69026<br>0·62301 | 1·39220<br>1·35197 | 0·0808<br>0·0810<br>0·0813<br>0·0814 | | |
| | | | | Mean 0·0810 | 1·4487 | 0·056 |
| Octyl Iodide, $C_8H_{17}I$. | 14<br>88 | 1·34096<br>1·25332 | 1·4922<br>1·4579 | 0·0467<br>0·0476<br>0·048 | | |
| | | | | 0·0475 | 0·7457 | 0·063 |
| Methylene Iodide, $CH_2I_2$. | 8<br>87 | 3·3480<br>3·1390 | 1·74935<br>1·69500 | 0·0425<br>0·0429<br>0·0442<br>0·0445 | | |
| | | | | 0·0440 | 0·29868 | 0·15 |
| Toluene, $C_7H_8$ ......... | 10·7<br>90 | 0·87532<br>0·79949 | 1·5028<br>1·45673 | 0·0677<br>0·0683<br>0·0688<br>0·0709 | | |
| | | | | 0·0688 | 1·1424 | 0·06 |
| Phenyl Chloride, $C_6H_5Cl$. | 9·6<br>89·2 | 1·1167<br>1·0302 | 1·53103<br>1·48731 | 0·0421<br>0·0533<br>0·0572<br>0·0543<br>0·0577 | | |
| | | | | 0·0540 | 0·8955 | 0·06 |
| Phenyl Bromide, $C_6H_5Br$. | 4·2<br>89·2 | 1·5100<br>1·39638 | 1·56845<br>1·52235 | 0·0458<br>0·0440<br>0·0464<br>0·0487<br>0·052 | | |
| | | | | 0·047 | 0·66225 | 0·071 |
| Phenyl Iodide, $C_6H_5I$. | 8<br>88 | 1·8482<br>1·7272 | 1·62755<br>1·58301 | 0·0444<br>0·0441<br>0·0450<br>0·0461<br>0·0465 | | |
| | | | | 0·0452 | 0·54107 | 0·083 |
| Aniline, $C_6H_7N$ ...... | 11·2<br>90·1 | 1·02792<br>0·95783 | 1·5912<br>1·54867 | 0·0490<br>0·0513<br>0·0546<br>0·0537<br>0·0538 | | |
| | | | | 0·0525 | 0·97283 | 0·054 |

Table II. (*continued*).

| Substance. | Temp. | Density. | $\mu_D$. | $\beta=\frac{(\mu-1)v-(\mu_1-1)v_1}{\mu-\mu_1}$. | $v$ at lower temp. | $\frac{\beta}{v}$. |
|---|---|---|---|---|---|---|
| Dimethylaniline,<br>$C_8H_{11}N$. | 8°<br>89·7 | 0·96688<br>0·89961 | 1·56535<br>1·52345 | 0·0610<br>0·0665<br>0·0671<br>0·0850 | | |
| | | | | 0·068 | 1·03425 | 0·065 |
| α-Naphthylamine,<br>$C_{10}H_9N$. | 51<br>88·4 | 1·10043<br>1·07207 | 1·67084<br>1·65209 | 0·060<br>0·0678<br>0·0704<br>0·0800 | | |
| | | | | 0·069 | 0·90873 | 0·076 |
| Ethyl Cinnamate ...... | 12·9<br>91·1 | 1·05560<br>0·98815 | 1·56351<br>1·52500 | 0·060<br>0·0663<br>0·0684<br>0·080 | | |
| | | | | 0·068 | 0·94733 | 0·071 |
| Acetyl-acetone ......... | 11<br>99·3 | 0·98506<br>0·89787 | 1·44493<br>1·39634 | 0·211<br>0·222<br>0·224<br>0·251<br>0·278 | | |
| | | | | 0·240 | 1·0152 | 0·235 |
| Methyl-acetyl-acetone. | 8·34<br>99·2 | 0·99189<br>0·90324 | 1·44210<br>1·39526 | 0·173<br>0·178<br>0·185<br>0·207 | | |
| | | | | 0·186 | 1·0081 | 0·185 |
| Ethyl-acetone-oxalate. | 17<br>100 | 1·12879<br>1·04109 | 1·46503<br>1·42617 | 0·0676<br>0·0700<br>0·0772<br>0·0760 | | |
| | | | | 0·0710 | 0·8859 | 0·080 |
| Ethyl-diaceto-acetate. | 17·6<br>99·8 | 1·09313<br>1·0675 | 1·45729<br>1·41932 | 0·0476<br>0·0479<br>0·0487<br>0·0530<br>0·0603 | | |
| | | | | 0·0515 | 0·9148 | 0·0564 |

Table II. *(continued)*.

| Substance. | Temp. | Density. | $\mu_D$. | $\beta=\dfrac{(u-1)v-(\mu_1-1)v_1}{\mu-\mu_1}$. | $v$ at lower temp. | $\dfrac{\beta}{v}$. |
|---|---|---|---|---|---|---|
| Diacetyl-acetone ..... | 60° | 1·04248 | 1·46691 | 0·292 | | |
| | 99·8 | 1·00615 | 1·44386 | 0·291 | | |
| | | | | 0·309 | | |
| | | | | 0·350 | | |
| | | | | 0·314 | 0·96146 | 0·326 |
| Allyl-acetyl-acetone ... | 13·5 | 0·97671 | 1·46156 | 0·1515 | | |
| | 99·2 | 0·89832 | 1·41868 | 0·1614 | | |
| | | | | 0·1680 | | |
| | | | | 0·1894 | | |
| | | | | 0·205 | | |
| | | | | 0·175 | 1·0238 | 0·1709 |

It may be objected that the average values obtained for $\beta$ and $\beta/v$ are much too small, seeing that other estimates of these quantities give much larger figures. The ratio

$$\frac{\text{actual volume of molecules}}{\text{apparent volume of liquid}}$$

is generally estimated to be about 0·2 or 0·3; that is, about four times greater than the value now found by the new hypothesis.

To this objection it may be replied:—

1. Prof. Tait has expressed the opinion that "the estimates hitherto made can hardly be called even rough approximations. But probably the particle does not occupy so much as 5 per cent. of its share of the whole content" *. This estimate is not far from the 6 per cent. yielded by the foregoing calculations.

2. It will be suggested at a later stage that the expressions which give 0·2 or 0·3 for the ratio $\beta/v$ probably measure, not the molecular volume itself, but that part of the apparent volume which may be called the molecular domain.

Postponing further consideration of this argument, we may inquire whether the value of $\beta$ is dependent on the particular temperatures employed in the observations. That is to say, presuming that it is a measure of molecular volume, does it show any change in value at higher or lower temperatures? Very few series of observations are accurate enough to stand the severe test imposed on them by an attempt to answer this question. Of the few that seem suitable, I shall give two examples, taken from the work of Ketteler*. From these it will appear that the answer varies, carbon disulphide showing a constant value for $\beta$ at different temperatures, while water gives a *diminishing* value as the temperature rises.

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* Tait, 'Properties of Matter,' p. 90.

Carbon Disulphide, $CS_2$.

| Temperature. | $v$. | $\mu_D$. | $\beta$. | $(\mu-1)(v-\beta)$. |
|---|---|---|---|---|
| $-20^\circ$ | 0·75582 | 1·65950 | 0·0476 | 0·46879 |
| $-10$ | 0·76442 | 1·65158 | 0·0476 | 0·46878 |
| 0 | 0·77314 | 1·64375 | ...... | 0·46874 |
| 10 | 0·78207 | 1·63593 | 0·046 | 0·46872 |
| 20 | 0·79131 | 1·62806 | 0·046 | 0·46873 |
| 30 | 0·80093 | 1·62004 | 0·0464 | 0·46871 |
| 40 | 0·85515 | 1·61187 | 0·0459 | 0·46871 |

Here it is evident that the value of $\beta$ remains practically constant through a range of 60° C. The values given were calculated from 0° as one of the temperatures in each case.

If $\beta$ has the meaning here assigned to it, the above measurements indicate that 1 gram of carbon disulphide actually occupies 0·046 cubic centimetre. Moreover, if we take the ratio $\beta/v$, we find it to be 0·062 at 0° C., which is again very near the average value yielded by the many liquids already given.

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* *Ann. Phys. Chem.* xxxv. p. 693.

Water.

| Temperature, | $v$. | $\mu_D$. | $\beta$ calculated from first. | $\beta$ calculated for each pair. |
|---|---|---|---|---|
| 20·9 | 1·00196 | 1·33287 | ...... | ·204 |
| 31·0 | 1·0044 | 1·33177 | 0·204 | ·114 |
| 56·0 | 1·0149 | 1·32776 | 0·150 | ·085 |
| 87·0 | 1·0336 | 1·32107 | 0·114 | ·067 |
| 94·0 | 1·0386 | 1·31943 | 0·108 | |

The result here is quite different from that shown by carbon disulphide; $\beta$ varies with every change in the temperature. It is given in two columns, the first containing values obtained by taking each observation in conjunction with that at the lowest temperature. The next column contains values obtained by taking each pair of observations. This last series is the more suggestive.

1st. It shows $\beta$ to be *diminishing* as the temperature rises, and gives the value it has between 87° and 94°. At this temperature, where the water is approaching its boiling-point, the value of $\beta$ becomes 0·067 cubic centim., a close approximation to that given by the other liquids.

2nd. The ratio $\beta/v$ at the high temperatures is 0·063, almost exactly the ratio 0·064 given by the other liquids.

These results are suggestive, and at once raise a question as to the meaning of the diminution in $\beta$ as the temperature rises towards boiling-point. Any one acquainted with recent researches on the physical properties of liquids will at once recall those of Ramsay and Shields on Molecular Complexity; those of Thorpe and Rodger on Viscosity of Liquids, &c., as bearing on this question. The investigations mentioned, along with others, have rendered it almost certain that the molecule of water is a complex of the form $nH_2O$, and that the value of $n$ in this expression diminishes as the temperature rises. Consequently the high value now found for the volume of the water molecule, as measured by $\beta$, appears to be another indication of its greater molecular complexity, and the fall towards normal value as boiling-point is approached points to a molecular simplification as indicated by the other methods.

Somewhat similar, though more erratic, is the available evidence with regard to other liquids of known molecular complexity, such as the alcohols and acetic acid. The figures are not now quoted, as they must be redetermined with greater accuracy and perfect exclusion of atmospheric moisture during the experiments.

We may now test the value of $\beta$ in another way. It has already been mentioned that the ordinary Gladstone expression fails to deal with the transition from liquid to gas, and the suggestion is now made that the discrepancy is due to the neglect of the volume of the particles, a quantity which practically vanishes in the case of vapours.

The question arises, will the value of $\beta$ deduced from a liquid bring the liquid and gaseous numbers into agreement? Not many observations are available for this comparison. Obviously the same specimen ought to serve for the liquid and vapour. The work of Lorenz* and Prytz almost exhausts the published data of this sort.

Lorenz gives two observations on the liquid at different temperatures, and also an observation on the vapour formed by the liquid. Unfortunately Lorenz selected the temperatures of 10° and 20° C. for the observations on the liquids, which are too near one another to afford a very satisfactory basis for calculating $\beta$. Notwithstanding this, the results as shown in the following table (p. 683) are very encouraging.

This table shows that the difference between the specific refraction of a liquid and its vapour as calculated by the Gladstone expression may be 10 per cent. of the whole; also that if the value of $\beta$ as calculated from the liquid be employed in the modification now proposed, the difference between the liquid and vapour falls to less than 1 per cent. With a more accurate estimate of $\beta$ this difference might be still further reduced. The modified expression gives practically a constant for both liquid and vapour.

One remark ought to be made. The value of $\beta$ for carbon

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* Wied. *Ann.* 1880.

| Substance. | Temp. | Specific Refraction $(\mu-1)v$. | | $\beta$ calculated from Liquid. | Specific Refraction $(\mu-1)(v-\beta)$. | |
|---|---|---|---|---|---|---|
| | | Liquid. | Vapour. | | Liquid. | Vapour. |
| Carbon Disulphide ... | 10° | ·4889 | ·4289 | 0·0886 | ·4334 | ·4289 |
| " " ... | 20 | ·4882 | | | | |
| Chloroform ............ | 10 | ·2979 | ·2681 | 0·0672 | ·2677 | ·2681 |
| " ............ | 20 | ·2975 | | | | |
| Ethyl Iodide ............ | 10 | ·2634 | ·2334 | 0·0685 | ·2282 | ·2334 |
| " " ............ | 20 | ·2629 | | | | |
| Ethyl Acetate ......... | 10 | ·4148 | ·401 | 0·030 | ·4035 | ·401 |
| " " ......... | 20 | ·4147 | | | | |
| Ethyl Ether ............ | 10 | ·4905 | ·4561 | 0·098 | ·4554 | ·4561 |
| " " ............ | 20 | ·4900 | | | | |

disulphide is much greater than that deduced from Ketteler's figures already quoted; a fact which is difficult to explain, though difference of specimen may have something to do with it.

There is another set of observations by which $\beta$ can be tested. Prytz has given data for nine liquids and their vapours; but as he only took one observation on the liquid his work is only available for calculating $\beta$ from the liquid and vapour values. This can be compared with the average values previously obtained.

| Substance. | $\beta$ calculated from Liquid and Gas. |
|---|---|
| Methyl Alcohol ............ | 0·09 |
| Ethylene Chloride ......... | 0·116 |
| Ethedene " ......... | 0·085 |
| Acetone ..................... | 0·091 |
| Methyl Acetate ........... | 0·0655 |
| Ethyl Formate ............ | 0·093 |
| Propyl Iodide .............. | 0·112 |
| Methyl Propionate ......... | 0·096 |
| Benzene........................ | 0·16 |

These values are slightly higher than those deduced from two observations on the liquid, but the difference is not great.

A *prima facie* case having been shown for attaching some physical significance to the symbol $\beta$, it appeared probable that the values for different substances would show definite relationships between themselves; or that the value of $\beta$ for a given substance would be related to the value of $v$ at the freezing, boiling, or critical temperature.

Of these the boiling-point is the one for which data are mostly available, and a little examination suggested a close relation between the absolute temperature of the boiling-point and the two volumes $v$ and $\beta$. It may conveniently be written

$$\beta \propto \frac{v_T}{\sqrt{T}}.$$

For the Centigrade scale the relation indicated seems to approach one of equality.

There are ten substances for which $\beta$, $v_T$, and T are known with sufficient (or apparently sufficient) accuracy. The above equation is here used to find the value of $\beta$ from $v$ and T, and the value so obtained is compared with that given by the optical data.

The following table shows that the results are in fair agreement, if we remember that the three data compared together are mostly due to different observers using different specimens.

| Substance. | $v_T$. | $\sqrt{T}$. | $v_T \div \sqrt{T}$ | $\beta$ from refraction. |
|---|---|---|---|---|
| Heptane ............... | 1·629 | 19·3 | 0·084 | 0·081 |
| Carbon Disulphide ... | 0·818 | 17·89 | 0·0457 | 0·0460 |
| Aniline .................. | 1·146 | 21·2 | 0·054 | 0·0525 |
| Toluene ................. | 1·282 | 19·62 | 0·065 | 0·068 |
| Water .................. | 1·043 | 19·34 | 0·054 | { 0·067<br>0·060 ? |
| Phenyl Chloride ...... | 1·044 | 20·1 | 0·052 | 0·054 |
| Phenyl Bromide ...... | 0·766 | 20·7 | 0·0365 | 0·047 |
| Phenyl Iodide ......... | 0·6388 | 21·5 | 0·03 | 0·045 |
| Ethyl Cinnamate ...... | 1·2005 | 23·15 | 0·052 | 0·068 |
| Ethylene Dibromide... | 0·5178 | 20·13 | 0·026 | 0·031 |

Many other figures might be given but they are of inferior accuracy, and ought not to be placed along with those just quoted. The examples are sufficient to establish a case for further inquiry, inasmuch as the agreement is close enough in six or seven cases to preclude the notion of accidental coincidence.

If additional data confirm the foregoing result, it affords us another method of calculating the quantity $\beta$ when the boiling-point and the density at that temperature are known. I propose to get $\beta$ for other substances by this method, and test several deductions by the result. It is evident, on general grounds, that values of $\beta$ calculated by this method will be of the same order of magnitude as that given by the optical data. All ordinary liquids boil between, say, 50° and 300° Centigrade, or 320° and 470° absolute; and the square roots range between 18 and 22, with average about 19, which is fairly near the average ratio for $v_1/\beta$.

It is hardly necessary to point out that this relation may possibly supply a hint as to the unknown law between volume-relationships of liquids and the temperatures. For example, I was tempted to compare the varying value of $\beta$ in the case of water with its very varied coefficient of thermal expansion $\alpha$.

Apparently, these two quantities are inversely proportional, as shown in the following table by the comparative constancy of the product $\beta \times \alpha$.

Water.

| Temperature-range. | $\beta$. | $\alpha$. | $\beta \times \alpha$. |
|---|---|---|---|
| 20°·9 to 31° | 0·203 | ·00025 | ·0000505 |
| 31 " 56 | 0·144 | ·0004 | ·0000576 |
| 56 " 87 | 0·082 | ·00059 | ·0000482 |
| 87 " 94 | 0·067 | ·00072 | ·0000482 |

In reading this table the approximate character of the value for $\beta$ must be kept in mind. The last column then indicates the probability of some connexion between $\beta$ and $\alpha$. $\alpha$ is calculated from data given by Thorpe.

Slight though this evidence may appear it seems to me to warrant further careful investigation, in view of the desirability of finding some method of obtaining a general law governing the thermal expansion of liquids, and the admitted difficulty of the problem.

*Note.*—I have quite recently calculated the value of $\beta$ from another series of figures due to Ketteler, and quoted in Landolt and Bornstein's tables. The general tendency is as above, but the product $\beta \times \alpha$ varies from $\cdot 0_4 428$ to $\cdot 0_4 600$. There is perhaps internal evidence, however, for regarding the figures as less accurate than the foregoing, so that I let the matter stand, subject to correction.

Summing up the general results obtained so far, we find:—

1. In simple liquids the quantity $\beta$ lies between narrow limits, the average being 0·05 cubic centim.
2. The ratio $\beta/v$ averages 0·064. That is, the actual volume of the molecules is about 6 per cent. of the apparent volume.
3. Liquids known to have exceptional physical properties, such as water &c., give higher values of $\beta$ than usual. This higher value changes with temperature, and is probably a measure of molecular complexity.
4. There is reason to think that some liquids, like carbon disulphide, yield a constant value for $\beta$ at different temperatures.
5. The value of $\beta$ given by a liquid enables us to apply the Gladstone formula (amended) during the transition from the liquid to the gaseous state.
6. There are grounds for believing that the value of $\beta$ is related to other volume-relationships of the substance, as, for example, the specific volume at the boiling-point.
7. In some cases there may be a connexion between $\beta$ and the coefficient of thermal expansion.

A further argument for the introduction of the quantity $\beta$ is the fact that it will remove certain anomalies in molecular refractions, bringing the value for hydrogen, chlorine, &c. into harmony with that given by the gaseous elements. This point, together with others of a like nature, is reserved for another paper.

So far as the suggestions thrown out are probable, it would appear that "the actual volume of the particles" is not a correct expression for $\beta$. In the case of water, $\beta$ has a varying value, which is attributed to the resolution of its complex molecule into simpler forms. But such resolution could not diminish the volume of the particles, unless we mean by this phrase "the true volume of the atoms + the inter-atomic space." If we imagine a surface drawn to enclose the molecule, it will include such space as lies between the atoms in that molecule. Similarly, when two molecules coalesce to form one of greater complexity the space occupied by the two is greater than before. They do not actually touch, so that the enclosing surface has a greater volume than twice that which encloses one molecule.

The results obtained so far show that the modified Gladstone expression promises to cover all ranges of density*. This wide range of applicability is obtained by emphasizing the volume-relationships involved in the formula—a fact which acquires further significance when we remember that it is as a measure of a volume that the Gladstone expression has proved so useful. For the specific refraction of a substance, $(\mu-1)v$, is evidently a fractional part of the specific volume $v$. Moreover, both Dufet (*Journ. de Phys.* 1885) and Sutherland (Phil. Mag. 1888), in developing a theoretical basis for the Gladstone law, have shown that "volume of molecules" is involved, though the exact definition of the phrase is not arrived at.

It seemed worth while asking whether this fractional part of the volume had a physical meaning. If the quantity $\beta$ may be regarded as a measure of true molecular volume, and there still remain a certain element of volume to be measured, it will most probably be found by accepting a well-known kinetic constitution for the liquids. If temperature be constant, we may assume that each molecule of a liquid vibrates as a whole over a certain region called its domain, the centre of this region being defined as the centre of the molecule when in its mean position.

The extent of the domain, and the relation between it and the total volume, will depend on the energy of molecular motion, and on the law of molecular force with regard to distance.

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* Except perhaps in the case of certain solids. See data for refraction of solids collected in the paper by Dr. Gladstone and myself already mentioned, Chem. Soc. Trans. 1895, p. 831.

Thus the apparent volume is made up of fractional parts, one of which may be called the sum of the volumes of the molecules, another the sum of the volumes of the domains, and a third the interstitial spaces. A satisfactory theory for evaluating these can perhaps not be found till more is known of the magnitude and law of the molecular forces, but an empirical examination suggested that $(\mu-1)v$ might possibly serve as a basis for finding the domain. At any rate it gives by transposition a part of $v$ which fairly answers to the only criterion of the domain which I can lay down.

Nothing is known as to possible change of the dimensions of the molecules themselves, but it seems highly probable that the domain of a given substance will most certainly differ under different physical conditions. Still further does it seem probable that the domain of different substances, heated between the same temperature-limits, may change in the same ratio. Figures in the tables which follow will prove this for the new expression, to what may be called a first approximation.

The transformation referred to is

$$(\mu-1)v=\mu\left[v-\frac{v}{\mu}\right],$$

the value of the square bracket on the right being equal to $\frac{\mu-1}{\mu}.v.$

It was evident to me, and will be to any one familiar with the data given by molecular refractions, that this last expression gives a fraction of $v$ tolerably near that obtained by the use of the other well-known expression

$$\frac{\mu^2-1}{\mu^2+2}.v.$$

I can best illustrate this by taking a table from a lecture on the "Range of Molecular Forces" delivered to the Chemical Society by Rücker (Chem. Soc. Journ. 1888, p. 253).

Using Hopkinson's data, Rücker compares the values of

$$\frac{K-1}{K+2} \text{ and } \frac{\mu^2-1}{\mu^2+2}$$

for five substances (K = specific inductive capacity). His object is to show that the figures justify well-known theories due to Clausius, Clerk-Maxwell, and others. Assumptions underlying these expressions make them a measure of the ratio

$$\frac{\text{true volume of molecules}}{\text{apparent volume of liquid}},$$

though the expression "true volume of molecules" is a quantity depending on what is better known as the "diameter of the molecule," *i. e.* the smallest distance between the centres of molecules.

The table is quoted bodily, with an additional column to show the value of $\frac{\mu-1}{\mu}$, this last being the factor of $v$ in the square bracket of the transposed expression.

| Substance. | Formula. | K. | $\mu^2$. | $\frac{K-1}{K+2}$. | $\frac{\mu^2-1}{\mu^2+2}$. | $\frac{\mu-1}{\mu}$. |
|---|---|---|---|---|---|---|
| Amylene ...... | $C_5H_{10}$. | 2·05 | 1·9044 | 0·260 | 0·232 | 0·245 |
| Benzol ......... | $C_6H_6$. | 2·38 | 2·2614 | 0·315 | 0·296 | 0·334 |
| Toluol ......... | $C_7H_8$. | 2·42 | 2·2470 | 0·321 | 0·291 | 0·333 |
| Xylol............ | $C_8H_{10}$. | 2·39 | 2·2238 | 0·317 | 0·290 | 0·329 |
| Cymol ......... | $C_{10}H_{12}$. | 2·25 | 2·2254 | 0·294 | 0·290 | 0·295 |

Here it is evident that there is a close agreement among the three sets of figures, amply sufficient to justify further examination. So far as differences occur, $\frac{\mu-1}{\mu}$ is nearer $\frac{K-1}{K+2}$ than is $\frac{\mu^2-1}{\mu^2+2}$.

In pursuing this comparison I shall introduce $\beta$, so that

$$(\mu-1)(v-\beta)=\mu\left[(v-\beta)-\frac{v-\beta}{\mu}\right].$$

The square bracket is equal to

$$\frac{\mu-1}{\mu}(v-\beta),$$

and it is under this head that the figures appear in the following tables :—

Carbon Disulphide.

| Temperature. | $\frac{\mu^2-1}{\mu^2+2}\cdot v$. | $\frac{\mu-1}{\mu}\cdot(v-\beta)$. | $\frac{v-\beta}{\mu}$. | $\frac{v-\beta}{\mu}$ calculated. |
|---|---|---|---|---|
| −20° | 0·2788 | 0·2821 | 0·4277 | 0·4259 |
| −10 | 0·2793 | 0·2835 | 0·4349 | 0·4341 |
| 0 | 0·2798 | 0·2847 | 0·4424 | 0 |
| 10 | 0·2803 | 0·2867 | 0·4494 | 0·4502 |
| 20 | 0·2808 | 0·2875 | 0·4578 | 0·4581 |
| 30 | 0·2813 | 0·2890 | 0·4659 | 0·4659 |
| 40 | 0·2819 | 0·2904 | 0·4746 | 0·4735 |

The experimental data are Ketteler's, and have already been given.

On comparing columns 2 and 3, it is seen that the figures are remarkably close to one another. The difference is just over 1 per cent. at −20°, and though it increases as the temperature rises, it only just exceeds 3 per cent. at +40° C.

Column 4 contains the values of the second term in the bracket, or $\frac{1}{\mu}$th of $v-\beta$; and column 5 contains the "calculated" values for the same expression. The calculation is made by taking the value at 0° C. and multiplying by the square root of the ratio of absolute temperatures. Thus the value at −20° is equal to

$$0{\cdot}4424\times\sqrt{\frac{254}{274}}=0{\cdot}4259.$$

I was led to try this by the results obtained in the first part of the present paper, and the extremely close approximation of the calculated to the other numbers is surely of some importance. The quantity $\frac{v-\beta}{\mu}$ will be referred to as the interstitial space.

The next table contains data for substances already mentioned.

| Substance. | Temp. | $\frac{\mu-1}{\mu}(v-\beta)$. | $\frac{\mu^2-1}{\mu^2+2}v$. | Difference. | | Ratio of New Values. |
|---|---|---|---|---|---|---|
| | | | | Actual. | per cent. | |
| Thymol ……………… | 24·4° | 0·39022 | 0·3110 | 0·079 | 20 | 1·0154 |
| " | 77 | 0·39542 | 0·3124 | … | … | |
| Cinnamic Alcohol…… | 24·8 | 0·3208 | 0·3168 | 0·004 | 1·2 | 1·0152 |
| " | 77 | 0·3261 | 0·3182 | … | … | |
| Anethol ……………… | 14·9 | 0·3378 | 0·3241 | 0·0137 | 4 | 1·0199 |
| " | 77 | 0·3445 | 0·3260 | … | … | |
| α-Methyl α-Naphthol | 14 | 0·3255 | 0·3182 | 0·007 | 2 | 1·0187 |
| " " | 77 | 0·3316 | 0·3202 | … | … | |
| Dimethyl Naphthalene | 16 | 0·3377 | 0·3395 | −0·0018 | −0·6 | |
| | 78 | 0·3438 | 0·3412 | | | |
| Heptane……………… | 12 | 0·3853 | 0·3451 | 0·04 | 10 | 1·030 |
| " | 89 | 0·3968 | 0·3471 | … | … | |
| Octyl Iodide ………… | 14 | 0·2303 | 0·2164 | 0·014 | 6 | 1·024 |
| " ………… | 88 | 0·2358 | 0·2177 | … | −11 | |
| Methylene Iodide…… | 8 | 0·1091 | 0·1216 | −0·012 | … | 1·0318 |
| " ……… | 87 | 0·1126 | 0·1225 | … | … | |
| Toluene ……………… | 10·7 | 0·3591 | 0·3376 | 0·021 | 6 | 1·0312 |
| " … …………… | 90·3 | 0·3703 | 0·3403 | … | … | |
| Phenyl Chloride …… | 9·6 | 0·2922 | 0·2771 | 0·015 | 5 | 1·029 |
| " …… | 89 | 0·3007 | 0·2793 | … | … | |
| Phenyl Bromide …… | 4·2 | 0·2230 | 0·2168 | 0·006 | 3 | 1·031 |
| " …… | 89·2 | 0·2296 | 0·2185 | … | … | |
| Phenyl Iodide ……… | 8 | 0·1913 | 0·1919 | −0·0006 | −0·3 | 1·028 |
| " ……… | 88 | 0·1967 | 0·1935 | … | … | |
| Aniline ……………… | 11·2 | 0·3417 | 0·3288 | 0·013 | 4 | 1·0273 |
| " ……………… | 90·1 | 0·3511 | 0·3319 | … | … | |
| Dimethylaniline …… | 8 | 0·3462 | 0·3336 | 0·0126 | 3·6 | 1·0304 |
| " ……………… | 89·7 | 0·3567 | 0·3363 | … | … | |
| Ethyl Cinnamate …… | 12·9 | 0·3169 | 0·4210 | 0·104 | 33 | 1·0255 |
| " | 91·1 | 0·3250 | 0·4378 | … | … | |
| α-Naphthylamine …… | 51 | 0·3370 | 0·3396 | −0·0026 | 0·8 | |
| " … .. | 88·4 | 0·3408 | 0·3409 | … | … | |
| Acetyl-acetone ……… | 11 | 0·2387 | 0·2702 | 0·0315 | 13 | 1·0349 |
| " ……… | 99·3 | 0·2488 | 0·2678 | … | … | |
| Methyl-acetyl-acetone | 8·34 | 0·2560 | 0·2668 | −0·0108 | 4 | 1·033 |
| " … | 99·2 | 0·2800 | 0·2656 | … | … | |
| Ethyl-acetyl-acetone… | 15·4 | | | | | |
| " … | 100·3 | | | | | |
| Ethyl-acetone-oxalate | 17·0 | 0·2587 | 0·2449 | 0·0138 | 5 | 1·0272 |
| " | 100·0 | 0·2665 | 0·2545 | … | … | |
| Ethyl-diacetol-acetate | 17·6 | 0·2710 | 0·2493 | 0·0217 | 8 | 1·0267 |
| " | 99·8 | 0·2615 | 0·2367 | … | … | |
| Diacetyl-acetone …… | 60·0 | 0·2065 | 0·2667 | −0·0602 | 29 | |
| " ……… | 99·8 | 0·2089 | 0·2639 | … | … | |
| Allyl-acetyl-acetone … | 13·5 | 0·2681 | 0·2812 | −0·0131 | 5 | 1·0322 |
| | 99·2 | 0·2769 | 0·2809 | … | … | |
| Ethyl Acetate ……… | 10 | 0·2909 | 0·2546 | 0·0363 | 12 | 1·0039 |
| " ……… | 20 | 0·2920 | 0·2549 | … | … | |
| Chloroform ………… | 10 | 0·1848 | 0·1990 | 0·0058 | 3 | 1·0040 |
| " ………… | 20 | 0·1855 | 0·1791 | … | … | |
| Ethyl Alcohol ……… | 10 | 0·3266 | 0·2804 | 0·046 | 14 | 1·0029 |
| " ……… | 20 | 0·3276 | 0·2807 | … | … | |
| Ethyl Iodide………… | 10 | 0·1514 | 0·1557 | −0·0043 | 3 | 1·0046 |
| " ………… | 20 | 0·1521 | 0·1558 | … | … | |
| Carbon Disulphide … | 10 | 0·2668 | 0·2805 | −0·013 | 5 | 1·0049 |
| " ………… | 20 | 0·2681 | 0·2809 | … | … | |

On examining this table we find that the new expression gives results which very fairly agree with those derived from Lorentz's formula. The average difference between the two is about 5 per cent., a difference not greater than that which would be yielded by the expressions of Clausius and Maxwell. So far as this agreement goes we may regard

$$\frac{\mu-1}{\mu}(v-\beta)$$

as a fair approximation to a volume quantity, which I may be allowed to call "molecular domain."

The value, as given by either formula, increases with the temperature. The highest increase by the $\mu^2$ expression is about one per cent. in the case of aniline. Whether such an increase could be attributed to the molecule proper, is an unsolved problem. It is usual to regard the values yielded by the Lorentz formula as more constant than here appears, but the figures are too numerous and too reliable to leave any doubt about the magnitude of the change.

As I have already said, it seems probable that domains will change in the same ratio between the same temperature limits. This can be tested for the new expression by the figures in the last column, which gives the ratio of the two values for

$$(v-\beta)-\frac{v-\beta}{\mu} \text{ or } \frac{\mu-1}{\mu}(v-\beta)$$

found at two temperatures.

To facilitate comparison, the substances are arranged in groups, marked off by a line. The members of each group are heated between approximately the same temperatures. Thus thymol is heated between 24°·4 and 77°, cinnamic alcohol between 24°·8 and 77°. The domain of the first increases in the ratio 1·0154, that of the second in the ratio 1·0152.

The members of the large group beginning with heptane and ending with ethyl cinnamate are heated between limits the lower of which lies between 4° and 12°, while the upper limit lies between 87° and 90°. The new domain rises generally in this group by 3 per cent. Out of the ten substances, seven give a ratio of increase very near to 1·030, the other three are near 1·027.

The next group includes eight substances heated between, say, 12° and 100°. Three give ratios close to 1·033, two yield 1·027. The last group is heated from 10° to 20° only, and gives ratios close to 1·004, except in the case of alcohol.

These results seem to afford a reasonable presumption in favour of the figures being regarded as a measure of domain. There is evidently a tendency for the ratio of increase to be the same for the different liquids, although their densities vary in the ratio of 5 to 1. It is surely improbable that molecules of very varying atomic structure should have the same temperature increase, but the same improbability does not attach to "domain."

There is, however, one aspect of this question which may prove to be still more important. It may be objected that the empirical* expression here used for obtaining the domain is too fanciful to be regarded with serious consideration. It may further be pointed out that it is equivalent to

$$(\mu-1)(v-\beta)\times\frac{1}{\mu},$$

as we have seen, and that the first two factors give a constant. Any relationships like those just alluded to must therefore be dependent on a more or less common temperature function for the refractive index.

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[*] In the June number of the Chem. Soc. Journal appears an abstract of a paper by W. F. Edwards (American Chem. Journ.), who obtains the expression now proposed, as a new formula for specific refraction, thus:— If V and $V_1$ are the velocities of light in space and the substance respectively, $\mu=\frac{V}{V_1}$. Let $A=V-V_1$, then $A=\frac{\mu-1}{\mu}V$. If the difference A is proportional to the amount of substance, and assuming as unit one gramme of substance in 1 cub. centim., and that X is the retardation of velocity for unit substance, then

$$X=\frac{\mu-1}{\mu}V\times\frac{1}{d}.$$

This is the same expression as that I propose for domain, multiplied by V. As will be seen from my tables, and as Edwards shows, the value of X is not a constant. It cannot therefore serve as a measure for specific refraction unless under stated conditions of temperature. He promises to return to this, but will, I believe, only find the solution by substituting "volume of domain" for volume of substance. As will be seen, I obtain his expression by a transformation of the Gladstone expression.

It is evident, apart from arithmetic error, that this must be so. But such an objection, while having weight against an expression obtained by the method we have pursued, at once raises a very suggestive question. Does the evidence really justify the idea that the refractive indices of various substances change in the same ratio between the same temperature limits? In other words, Is the ratio magnitude of the change independent of the nature of the liquid? The following table gives the evidence available. The substances quoted are those already dealt with, but the comparison deals directly with the refractive indices, and is therefore free from all objections which might be urged against the hypothesis of this paper.

To facilitate comparison, the substances are again divided into groups, the order being slightly different from that previously given. The refractive indices are given in column 3; column 4 gives the ratio of the two indices, which are slightly corrected in column 5. This is done by calculating from columns 2 and 3 the average change in the index per degree, as shown in column 6. The figure thus obtained is used to calculate the change of index for 80° exactly, which means an alteration of only a degree or two for most substances. The ratio in column 5 is calculated then for a common interval of 80°, and will be somewhat nearer the truth than the uncorrected ratio in column 4.

Column 7 gives the exponent of $\mu$ in the statement $\mu^x \propto \frac{1}{\mathrm{T}}$, where T is the absolute temperature. It therefore equals

$$\log\frac{\mathrm{T}_2}{\mathrm{T}_1} \div \log\frac{\mu_1}{\mu_2}.$$

The ratio $\frac{\mu_1}{\mu_2}$ is about 1·03, so that the different powers of it do not vary so much.

An examination of this table will show that for the same temperature limits there is a fair approach to constancy in the ratio $\frac{\mu_1}{\mu_2}$.

Thus the indices of the first seven substances all give

| Substance. | Temp. | $\mu$. | $\frac{\mu_1}{\mu_2}$. | $\mu_1 \div \mu_2$ corrected. | $\frac{\mu_1 - u_2}{T_2 - T_1}$. | $x = \text{lcg}\,\frac{T_2}{T_1} \div \log \frac{\mu_1}{\mu_2}$. |
|---|---|---|---|---|---|---|
| Heptane.................. | 12° | 1·3922 | 1·0297 | 1·0317 | ·000522 | 8·1 |
| " .................. | 89 | 1·35197 | | | | |
| Methylene Iodide...... | 8 | 1·74935 | 1·0321 | 1·0325 | ·000671 | 8·0 |
| " .................. | 87 | 1·69500 | | | | |
| Toluene.................. | 10·7 | 1·5028 | 1·0316 | 1·0318 | ·000576 | 8·05 |
| " .................. | 90 | 1·45673 | | | | |
| Phenyl Chloride ...... | 9·6 | 1·53103 | 1·0293 | 1·0295 | ·000546 | 8·84 |
| " ...... | 89·2 | 1·48731 | | | | |
| Acetyl-acetone ......... | 11 | 1·44493 | 1·0349 | 1·0314 | ·000552 | 7·92 |
| " ......... | 99·3 | 1·39634 | | | | |
| Methyl-acetyl-acetone | 8·34 | 1·4421 | 1·0334 | 1·0295 | ·000514 | 8·49 |
| " | 99·2 | 1·39526 | | | | |
| Ethyl-acetyl-acetone... | 15·4 | 1·44066 | 1·0324 | 1·0307 | ·000535 | 8·0 |
| " ... | 100·3 | 1·3952 | | | | |
| Phenyl Bromide ...... | 4·2 | 1·56845 | 1·0303 | 1·0285 | ·000543 | 9·46 |
| " ...... | 89·2 | 1·52235 | | | | |
| Phenyl Iodide ......... | 8 | 1·62755 | 1·0279 | 1·0279 | ·000557 | 9·17 |
| " ......... | 88 | 1·58301 | | | | |
| Aniline .................. | 11·2 | 1·5912 | 1·0274 | 1·0278 | ·000538 | 9·23 |
| " .................. | 90·1 | 1·5487 | | | | |
| Dimethylaniline ...... | 8 | 1·5583 | 1·0270 | 1·0265 | ·000510 | 9·6 |
| " ...... | 89·7 | 1·51704 | | | | |
| Ethyl-acetone-oxalate | 17 | 1·46503 | 1·0272 | 1·0262 | ·000536 | 9·35 |
| " ...... | 100 | 1·4263 | | | | |
| Ethyl-diaceto-acetate | 17·6 | 1·4573 | 1·0270 | 1·0261 | ·000463 | 9·29 |
| " ... | 99·8 | 1·4193 | | | | |
| Ethyl Cinnamate ...... | 12·9 | 1·5479 | 1·0253 | 1·0259 | ·000476 | 9·93 |
| " ...... | 91·1 | 1·5108 | | | | |
| Octyl Iodide ............ | 14·5 | 1·4922 | 1·0236 | 1·0254 | ·000463 | 9·99 |
| " ............ | 88·5 | 1·4579 | | | | |
| Thymol.................. | 24 | 1·5145 | 1·0154 | 1·0154 | ·000427 | 10·7 |
| " .................. | 77·3 | 1·4919 | | | | |
| Cinnamic Alcohol...... | 24·8 | 1·5731 | 1·0153 | 1·0153 | ·000447 | 10·6 |
| " ...... | 77·3 | 1·5494 | | | | |

ratios very near to 1·031. This is specially striking if we take particular cases like the first two on the list—heptane and methylene di-iodide—as shown in the following short table (p. 696).

It is also noteworthy that this same ratio (1·03) holds good in the case of those substances whose tendency to tautomerism is productive of anomalies. These are acetyl-acetone, methyl-acetyl-acetone, and ethyl-acetyl-acetone, which give abnormal values for $\beta$, and which differ from all other substances, even when tested by the Lorentz formula. Of course the ratio 1·03 is not preserved all the way down this group; the lower

| | Temp. | Density. | Between the same temp. limit. | |
|---|---|---|---|---|
| | | | Ratio of Densities. | Ratio of Indices. |
| Heptane ............... | 12° | 0·6903 | 1·11 | 1·0317 |
| " ............... | 89 | 0·6230 | | |
| Methyl Di-iodide..... | 8 | 3·348 | 1·07 | 1·0325 |
| " " ...... | 87 | 3·139 | | |

members fall to about 1·026. Whether this means only a slight departure from the other value, or whether it indicates a breakdown of the suggested constant relationship can only be decided when many more accurate temperature observations are obtainable. The ratio altogether breaks down in the case of such substances as water, which, as I have suggested, show special relations to refractive index by reason of varying molecular complexity.

The last column in the foregoing table gives the ratio of the logarithms of temperatures and indices. Further research may make this column more valuable than it now appears.

Taken altogether, the table affords ground for believing that there are close relationships between refractive index and temperature, and, further, that the ratio of change for a particular temperature interval may be the same for many different liquids.

The question then arises, whether this last relation is direct, or arises from some material property changing with the temperature? Is it possible that the velocity of light may vary with temperature, apart from any relation to material substances, or is the foregoing relationship dependent upon some molecular function like that suggested, that is "molecular domain?"

It seems impossible to answer the first part of this question. The second part can be judged by analogy, which would appear to suggest that a molecular function is more probable. Thus, one might expect that the kinetic energy of the particles is the property directly increased by rise of temperature, and that many or all other properties of the molecule are consequential upon that. The apparent volume of course increases. That fraction of the volume which is measured by

$$\frac{\mu^2-1}{\mu^2+2}v, \text{ or } \frac{\mu-1}{\mu}(v-\beta)$$

also increases, whatever it may be called. This constant fact appears to be a decided argument in favour of these expressions, giving "domain" and not "volume of matter" simply. But again, if the plea for "domain" be granted, there ought to be increase, not only when the liquid is heated, but also when it is changed into a vapour. This is actually the case for $\frac{\mu-1}{\mu}v-\beta$), the value of which increases in the ratio 1 to 1·4 or 1·5. This variability may be compared with that found by van der Waals for his constant "*b*" ('Continuity &c.', Phys. Soc. translation, p. 409).

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## *Correction.*

On page 286 of this volume (xiii.) of the 'Proceedings' in the report of the discussion upon Dr. Larmor's paper, Professor Lodge is represented as criticising Dr. Larmor's summary of Herr Wiener's paper. It appears that Professor Lodge intended to refer to asummary made some time ago by Herr Wiener and not by Dr. Larmor.

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